VOL. XXVIII 1915

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

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VOLUME XXVIII

TWENTY-EIGHTH GENERAL MEETING

PANAMA-PACIFIC INTERNATIONAL EXPOSITION
SAN FRANCISCO, SEPTEMBER 16, 17, 18, 1915

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LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.
1916

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VOLUME XXVIII 1915.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-EIGHTH GENERAL MEETING OF THE SOCIETY, HELD IN CONNECTION WITH THE PANAMA-PACIFIC INTERNATIONAL EXPOSITION AT SAN FRANCISCO, CALIFORNIA, SEPTEMBER 16, 17, 18, 1915.

Number of members registered, 30; number of guests registered, 33; total, 63.

PROCEEDINGS OF WEDNESDAY, SEPTEMBER 15.

Registration opened at 6.00 P. M. at the Clift Hotel. A meeting of the Board of Directors was held at 8.30 P. M., at the same place.

PROCEEDINGS OF THURSDAY, SEPTEMBER 16.

The meeting for the reading and discussion of papers was called to order at 10.00 A. M. in Hall F of the Auditorium at the Civic Center, San Francisco, President Lawrence Addicks in the Chair.

Papers by W. H. Wills, Jr., and A. H. Schuyler (abstracted by Secretary Richards), F. T. Snyder (abstracted by Secretary Richards), W. R. Mott (abstracted by H. C. Parmelee), F. C. Frary and R. E. Porter (abstracted by Frary and Porter, read by Secretary Richards), R. S. Bosworth (abstracted by Dr. S. C. Lind), A. G. Betts (abstracted by President Addicks), C. W. Bennett, C. C. Rose and L. G. Tinkler (read by title), F. M. Frederiksen (abstracted by L. H. Duschak), W. D. Bancroft (abstracted by L. H. Duschak), and W. D. Bancroft (abstracted

by L. H. Duschak) were presented and discussed as printed in full in these Transactions.

In the evening at 7.00 P. M. a complimentary dinner was given to visiting members and ladies, as guests of the Local Members of the Society, at the Techau Tavern. Mr. Chas. Butters presided ably as toast-master, and responses were made by President Addicks, Dr. F. C. Cottrell, C. J. Reed, Secretary Richards and Dr. J. F. Hildebrand.

PROCEEDINGS OF FRIDAY, SEPTEMBER 17.

The first meeting was a Joint Session with the American Institute of Mining Engineers in the Auditorium of their Headquarters, at the Bellevue Hotel, San Francisco. President L. Addicks, of the American Electrochemical Society, presided. The session was numerously attended and was called to order at 9.00 A. M.

Papers by Percy A. Boeck (abstracted by Mr. Krieger), R. S. Wile (read by title), D. A. Lyon and R. M. Keeney (presented by D. A. Lyon), G. H. Clevenger, F. R. Pyne (abstracted by Secretary Richards), W. P. Davey (read by title), L. Addicks, and R. R. Goodrich (abstracted by L. Addicks), were presented and discussed and are printed in full in these Transactions, with the exception of paper by R. R. Goodrich, which has been published in full by the American Institute of Mining Engineers.

At 12.30 P. M. the members of this Society joined in luncheon with the members of the American Institute of Mining Engineers, at the Clift Hotel, approximately 150 being present.

The afternoon session was a Joint Session with the American Institute of Electrical Engineers at the Native Sons Hall, San Francisco, Cal. It was called to order at 2.00 P. M., President Carty, of the American Institute of Electrical Engineers, in the Chair.

Papers were read by C. H. Aldrich (presented by Mr. H. F. Fischer), S. L. Foster, and J. W. Beckman, and are printed in full in these Transactions with the exception of the paper of Mr. Foster, which is printed in abstract. The full text of Mr. Foster's paper may be found in the Transactions of the American Institute of Electrical Engineers. In connection with Mr. Aldrich's paper, Dr. F. C. Cottrell described the large scale

experiments with the 1,000,000 volt, 1,000 kilowatt apparatus located in the Panama-Pacific Exposition Grounds, with the object of dissipating fog and investigating very high tension phenomena.

PROCEEDINGS OF SATURDAY, SEPTEMBER 18.

EXPOSITION DAY.

Members and guests assembled at 10.00 A. M. in the Mines and Metallurgy Palace at a platform opposite the Bureau of Mines exhibit, for formal presentation of a medal commemorating the meeting of the Society at the Exposition. Mr. Charles Butters presided, and introduced the speakers with well-chosen remarks.

Other addresses were then made by Chas. E. van Barneveld, Chief of the Department of Mines and Metallurgy, Mr. Vogelsang, representing officially the Panama-Pacific Exposition, who made the presentation of the medal, and by President Addicks, who received the medal for the Society. The addresses were substantially as follows:

Mr. Charles Butters: Ladies and gentlemen: There is a small attendance here this morning, but those of us who know of the work of the Society do not feel at all embarrassed. We of the Local Committee are pleased to welcome our visiting members, and I am sure what has been gathered here at this Exposition, and especially what has been done for us by Mr. Charles E. van Barneveld, chief of the department of mines and metallurgy, formerly professor of mining of the University of Minnesota, and now professor of mining of the University of California, is highly appreciated. It is remarkable that he has been able to gather such a wonderful collection representing the mining and metallurgy of the United States, and for this collection of things with which we are so familiar and in which we are all so much interested, I am sure we are all indebted to him. Mr. van Barneveld will welcome the Society to this building.

Mr. Chas. E. van Barneveld: One of the pleasantest duties of the Exposition period for those who have been actively engaged in the building of the Exposition is to welcome to it the thoughtful man, the scientific man, the man whose ideas and creations are really responsible for the fact that we can show so

many wonders to the public. An exposition such as this is a very wonderful thing, a wonderful lesson in co-operation. What the designers and builders of this Exposition tried to do was to create a thing of beauty, to appeal to the sense of color and form in the grounds and buildings; then to bring together in these various buildings a correct representation of the achievements of the last ten years in the Arts and Crafts and in the Sciences.

We have tried as far as possible to relegate the commercial to the background and to make this Exposition truly educational. When the miner and the metallurgist, in response to an invitation to participate, has objected, saying that he had nothing to sell, we have asked him to look at this Exposition as a large university where each industry in its turn acts as host, not to its own members but to the rest of the world. And so the mining, metallurgical and chemical industries of this country have fulfilled their functions of host to all the other applied sciences, industries, arts and crafts. While you may not be able to see such direct and definite benefits coming to you as the manufacturer of automobiles or watches or pottery receives from his exhibits, you have the satisfaction of knowing that hundreds of thousands of people have studied them and have been impressed with the tremendous importance of the basic industry of the country, impressed with the interdependence of agriculture, mining, metallurgy, manufacturing and transportation.

You will probably realize that I hoped for a better metallurgical representation than you will find in this building. In view of the conditions in the industrial world I feel very well satisfied with the results. The Co-operative Metallurgical Exhibit obtained through the instrumentality of the U. S. Bureau of Mines and its efficient corps of workers, some of whom are members of your Society, is instructive and well worked out. It has attracted a good deal of attention. Anyone who is willing to look into it will be led through the various steps of sampling, analysis and experimentation on one side of the block, while the cyanide process is illustrated on a fair scale on the other side. The U. S. Steel Corporation's and the Anaconda Copper Mining Company's exhibits of metallurgical processes and products are particularly worthy of your careful attention.

Many visitors have asked me: "What is the difference between a mining and a metallurgical engineer?" In explaining this I have often pointed to the columns of cubes in the Anaconda Copper Mining Company's space in the next block. It consists of four glass cubes. The lowest one contains one ton of low-grade crushed ore. The next one shows the effect of concentration—mechanical enrichment. The third one shows the effect of practical application of chemistry in the arts—shows the matte resulting from the smelting of the concentrates. Finally, on top is a little cube representing the achievement of the metallurgist in producing the metal of commerce. Many visitors have commented on the lessons they have learned in this Palace; it has been a revelation to them to learn of the multiplicity of interests that must work in harmony in order to reduce the natural mineral resources of the country to a salable and usable commodity.

Gentlemen, in the name of the Exposition and also in my own behalf I take pleasure in welcoming the American Electrochemical Society to the Panama-Pacific Exposition and to our Palace of Mines and Metallurgy.

Mr. Charles Butters: I am sure we are all interested in what Mr. van Barneveld said, and I now have the pleasure of introducing Mr. Charles Vogelsang, who is the Commissioner-General of the Panama-Pacific International Exposition. Mr. Vogelsang will present the medal which the Exposition has been kind enough to present to us, and that medal will be received by Mr. Lawrence Addicks, president of our Society. Mr. Addicks, I may say, is a member of the U. S. Naval Consulting Board, and that fact has more meaning behind it than the few words in which I state it may appear. The fact that a member of the Electrochemical Society has been appointed a member of the Naval Consulting Board means that the chemist and metallurgist, and engineers of the country, are more necessary to the defense of our country and in the preparation for defense than ever before. The war which is being carried on in Europe now is an engineer's war, a manufacturer's war. Strategy means less; the engineer and the chemist and the manufacturer mean more. It will mean much to our people and to our Government

to receive the help and assistance of the engineers who are appointed upon this Naval Consulting Board. (Applause.)

Mr. Charles A. Vogelsang: Mr. Chairman, ladies and gentlemen of the American Electrochemical Society: You are extremely welcome to our house. You represent here much of the bigness and dignity of our country and of its future, and we are especially glad to see you. In the words of the old Spanish hospitality—"Señor, enter my house, and all I have is yours." We desire to apply that expression especially to this Exposition. You honor us by coming here and holding a convention, a Congress which has brought together men from practically every State in our Union. While someone here commented upon you in a numerical sense, as not being so great this morning, I am reminded that there was a time in the history of our country when an important event occurred, when there were but thirteen colonies. But they represented something which has grown until we have the greatest nation in the world, which is now represented and typified at our most wonderful exposition, an exposition which we believe has had no parallel and which perhaps may never have a parallel. There may never be one grander or greater than this. It has brought together some 875 congresses and conventions, and among those who have attended these gatherings have been great thinkers and workers, men and women of the world, who are taking a leading part in its affairs.

This Exposition in itself is, we feel, worthy of the event it commemorates—the building of the Panama Canal. This Exposition is as much yours as ours, because the industry and profession you represent has had as much to do with bringing about this celebration as the State of California. Of course, the picture is staged in our house, we have provided the frame, but you have filled in the part which has made the picture so beautiful, and the various States which you represent have as much to do as the State of California in making the Canal and the picture. Therefore, this picture, this exposition, is yours as much as ours. When you leave this building you should go away with the feeling that you are not in the house of strangers, but in your own house.

As a representative of President Moore of the Exposition, it

is my pleasure and honor to present to the American Electrochemical Society a memento of your gathering here. In the history of your organization your holding a meeting here marks an important epoch, as does the holding of this exposition mark an important epoch in the history of the world. Here we are in peace and harmony, everything is set in a background of peace, and that is a most decided contrast to the picture of desolation and destruction and death across the water. You come here and hold this meeting in our city in connection with our Exposition, and we think it is timely. You have added your full quota to the very splendid men and women who have come here to give us such hearty and generous inspiration and help.

To commemorate this event we have a testimonial that is not rich in a monetary sense, nor studded with diamonds, neither is it made of gold, but it is made of that enduring quality of metal known as bronze, and is inscribed: "American Electrochemical Society, September 18, 1915. In Commemoration. Panama-Pacific International Exposition. San Francisco." Mr. Addicks, in behalf of President Moore, as director of the Exposition, I offer this to you as a token of our personal regard and of high esteem and appreciation of the Society you represent. (Applause.)

Mr. Lawrence Addicks: Mr. Chairman and gentlemen: I take great pleasure in accepting on behalf of the American Electrochemical Society the medal commemorating the holding of our Twenty-eighth General Meeting at San Francisco in connection with the Panama-Pacific International Exposition, and in acknowledging at the same time our appreciation of the courtesies extended by the officials of the Exposition.

Our Society is one of the younger of the National Scientific Bodies, and as such cannot boast the numerical strength of its older brothers, and, further, it represents a field—that of electrochemistry and allied subjects—which has not as yet found any considerable application on the Pacific Coast, so that the great majority of our members live at the other end of the country. While, therefore, but a representative few of our members have been able to attend a meeting at such distance, it seems the more desirable that we should learn of and discuss the oppor-

tunities offered by the far West to electrochemical industries. Several of the papers presented at the technical sessions just ended have dealt with this question, the results of which discussion should be to our mutual advantage.

I have been asked to outline briefly the formation of this Society and the field which it covers. While electrical phenomena were fairly well understood in the early part of the last century and Faraday conducted his classical researches in electrochemistry nearly a hundred years ago, with the exception of the electric telegraph and electroplating no industrial application of moment based upon electric action was made until the development of the dynamo in the sixties offered a practical method of converting mechanical into electrical energy.

As soon as this cheap source of current was available, replacing the primary cells utilizing chemical energy previously used as a source of power, the effect was felt in the immediate development of mechanical engineering, chemistry, metallurgy, and almost every other branch of engineering and science along new lines. Indeed, the modification of mechanical engineering was so marked that a new profession—that of electrical engineering—sprang into existence.. This, in turn, has developed with such rapidity that today an electrical engineer practices in one of many more or less distinct subdivisions of that profession.

In chemistry, electricity has furnished a directive force enabling reactions to be reversed. We have always been able to dissolve iron in sulphuric acid to form sulphate, but now, by the application of the electric current, we can reverse this procedure at will, obtaining iron and sulphuric acid from ferrous sulphate. In organic chemistry, a field of chemical synthesis has been opened up which may lead to the duplication of many of the products of nature, and perhaps the formation of some useful compounds which nature has not yet thought of.

In physics, the exploitation of the cathode rays, the remarkable properties of radium, and the development of wireless telegraphy have almost obliterated the dividing line between physics and chemistry, once so strongly marked, opening up a paradise for those who thrive on higher mathematics and shaking some of our most fundamental laws, as tried the alchemists of old.

In metallurgy, an equally great change has come about. Elec-

trolytic refining of metals produces a commercial product of a purity hitherto undreamed of. The great bulk of the copper of commerce is now so treated. The older processes for parting gold and silver have been virtually superseded. Some gold, lead, nickel and bismuth are being electrolytically refined; for the first time carbon-free iron has been produced, although no practical use has been as yet announced for such metal; and it seems likely that electrolytic or electric furnace zinc and tin will soon compete with the relatively impure products now marketed. These pure metals are offering new possibilities in the way of alloys, the properties of which are much affected by impurities.

The electric furnace has given us aluminum, a useful metal which a few years ago was but a chemical curiosity. It has produced graphite, carborundum, artificial gems, calcium carbides, and a host of other products now accepted as a matter of course.

Electroplating has enabled us to superimpose a layer of a noble metal which resists corrosion upon a foundation of a baser one which gives strength and cheapness.

In a similar way, electrotyping has revolutionized printing. The storage battery has made possible the transporting of electric energy to places otherwise inaccessible, such as the submerged submarine.

The strong oxidizing and reducing effects at the anode and cathode of an electrolytic cell have been utilized to produce bleaching agents, chlorine, alkalies, ozone, and many other products.

The fixation of atmospheric nitrogen has become an accomplished fact, and an inexhaustible source of plant food made available.

Further, electrochemical industries, being large consumers of power, tend to develop the water powers of this country. Niagara Falls is at present the center of such industries, but other localities are being developed.

It can be readily appreciated that work along these lines called for a certain knowledge of chemistry, electrical engineering and metallurgy, not possessed by those trained in any one of the separate branches, a matter which has been acknowledged in the last few years by the establishment at most of our technical schools

of special courses and laboratories in electrochemistry. In the same way men interested in this special field did not find themselves entirely at home in any of the three corresponding National Societies. This situation was recognized by three men—Dr. Carl Hering, Dr. E. F. Roeber and Mr. C. J. Reed—and in 1902 they were instrumental in organizing a representative conference in Philadelphia, which resulted in the formation of the American Electrochemical Society on April 2nd of that year, with over 350 members. This has steadily grown, until today there are about 1,400 members, about forty papers a year being presented and incorporated in the Transactions of the Society, of which over 10,000 pages have been published. The great diversity of the field covered is in itself a source of strength, in that it brings together men of widely different experience and points of view who would come in contact within none of the other societies. It is not probable that we shall ever grow to the size of the present mammoth engineering bodies who cater to the great numbers of men interested in such problems as transportation, communication, light and power, but it is a safe prophecy that it is perhaps chiefly within the legitimate domain of electrochemistry, or, more strictly speaking, physical chemistry—that many of our scientific discoveries of the future will be developed, whether it be in connection with the constitution of matter, the mechanism of life, or the unguessed wonders awaiting summons from the unexplored wave-lengths of energy lying between and beyond the regions we know as light, heat and electricity.

We therefore feel that the American Electrochemical Society has done its share in the industrial progress of the last few years, to which this great Exposition testifies on so magnificent a scale, and with which we feel it a privilege to be identified by the brief ceremony of this morning.

After these exercises were completed, the members and guests were invited to inspect particularly the exhibits of the Bureau of Mines, and of the Bureau of Standards in an adjoining building. A number of members visited the Norwegian Building upon receipt of an urgent invitation of Norwegian Commissioner

Gade, and were there very interestingly entertained by inspecting the exhibits and charts, etc., showing the development of electrochemical industries in Norway, and a very interesting motion picture performance showing in all its details the plant and operations, at Rjukan, of the Norwegian Saltpeter Company.

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ZWINGENBERGER, Otto K. (Jan. 27, '12) Chemist, Patent Dept., Roessler & Hasslacher Chem. Co., Perth Amboy, N. J.

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Weeks, F. D.
Weinstein, L. J.
Wettstein, T. F.
Whitaker, M. C.
White, J. G.
Wiechmann, F. G.
Wigglesworth, H.
Wilkinson, W. N.
Williams, A.
Williams, J. T.
Winship, W. E.
Witherell, C. S.
Wood, E. F.
Wright, Arthur
Zeller, R.

Niagara Falls—

Arison, W. H.
Barnes, Carl S.
Barton, P. P.
Bayard, R. A.
Becket, F. M.
Bliss, Wm. Lord
Brindley, G. F.
Callahan, J. F.
Carveth, H. R.
Cole, E. R.
Converse, V. G.
Cox, G. E.
Dunlap, O. E.
Edmands, I. R.
FitzGerald, F. A. J.
Fowler, R. E.
Frary, F. C.
Geyler, F. O.
Glaze, John B.
Griffith, J. R.
Hamann, A. M.
Harper, J. L.
Haskell, F. W.
Herzog, G. K.
Hinchley, A. T.
Horry, W. S.
Hooker, A. H.
Humbert, E. P.
Hutchins, Otis
Imlay, L. E.
Johnson, J. A.
Kellogg, H. W.
Kemmer, F. R.
Koethen, F. L.
Lavene, H. A.
Leffel, C. E.
Lidbury, F. A.
MacMahon, J.
MacMillan, J. R.

Maier, C. G.
Marshall, J. G.
Mauran, M.
McCullough, H. F.
McKnight, W. A.
Meredith, W. F.
Moritz, C. H.
Moyer, G. C.
Neuhaus, R.
Phillips, R.
Randall, J. W. H.
Rhodin, B. E. F.
Ross, Wm.
Rowland, J. M.
Russell, C. A.
Saunders, L. E.
Schlatter, H. C.
Sergeant, E. M.
Simmers, A. L.
Smith, A.
Smith, E. S.
Snowdon, R. C.
Speiden, E. C.
Stamps, F. A.
Stone, G. W.
Taylor, Chas. E
Tone, F. J.
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Wallace, W.
White, R. H.
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Acker, Chas. E.

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Main, W.

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Quintard, Edw.

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Johnston, F. A.
Johnston, W. A.

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Herreshoff, J. B.
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Smull, J. G.

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Hutchings, J. T.
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Berg, E. J.
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Langmuir, I.
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Seede, J. A.
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Pennock, J. D.

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Hunter, M. A.
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Patton, D. C.

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Harrington, E. I.

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Pickens, Rufus H.

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Browne, W. H.

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Marseilles, Wm. P.
Rockwell, Wm. F.

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Cope, F. T.

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Briggs, F. H.

Cincinnati—
Gerstle, John

Cleveland—
Brown, J. W.
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Chillas, R. B., Jr.
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Cook, Edw. B.
Crider, J. S.
Drefahl, L. C.
Fleming, S. H.
Graves, W. G.
Holmes, M. E.
Hyde, E. P.
Koehler, W.
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Pratt, E. B.
Seguine, Wm., Jr.
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Wellman, S. T.
Whitlock, E. H.
Woodward, J. M.

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Flowers, A. E.
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Dayton—
Clements, F. O.
Deeds, E. A.
Dorsey, H. G.
Niswonger, E. E.

Fostoria—
Downes, A. C.

Fremont—
Goodwin, J. H.
Ziegler, W. W.

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Moore, Wm. C.
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Middletown—
Ahlbrandt, G. F.

Napoleon—
Long, G. E.

Niles—
Richardson, E. A.

Oberlin—
Crafts, W. N.

Rittman—
Laib, Walter

Salem—
Davis, D. L.

Steubenville—
Homan, J. G.

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Shapiro, H.

Youngstown—
Danforth, Chas. W.
Grossmann, M. A.

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Ambler—
Coleman, Wm. B.

Ambridge—
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Aspinwall—
Hessom. B. F., Jr.

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Ober, J. E.

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Lewis, J. D.

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Hensen, Amil

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Fernekes, Gustave

Palmerton—
Holdstein, L. S.

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Blough, Earl

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Morgan, Leonard P.
Paul, H. N.
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Sadtler, S. P.
Sadtler, S. S.
Salom, P. G.
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Weisenburg, Andrew
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Wirt, Chas.

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Crabtree, F.
Davis, S. A.
Dewey, B.
Donkin, Wm. A.
Dougherty, J. W.
Flannery, Jas. J.
Gibson, C. B.
Goodale, S. L.
Hartley, R. H.
Hibbert, Harold
Hitchcock, H. K.
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James, J. H.
Kemery, P.
Kier, S. M.
Laughlin, H. H.
Lincoln, P. M.
McDonald, R. A.
McKinley, Jos.
Orr, R. S.
Osborne, L. A.
Page, G. S.
Pinkerton, A.
Pope, Chas. E.
Ray, H. C.
Rodman, H.
Sargent, G. W.
Schluederberg, C. G.
Slocum, F. L.
Speller, F. N.
Stewart, R. T.
Stupakoff, S. H.
Tiemann, H. P.
Turnock, L. C.
Uhlenhaut, F., Jr.
Vogt, C. C.
Wadsworth, F. L. O.
Webb, Z.
Wiley, B.

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Boericke, G.
Stein, W. M.

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Giles, I. K.
Parker, Jas. H.

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McDonald, F.

Scranton—
Bryden, C. L.

Sharon—
Kranz, W. G.

South Bethlehem—
Buck, C. A.
Callen, A. S.
Franklin, W. S.
Lomax, C. S.
MacNutt, B.
Richards, J. W.
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Seyfert, S. S.

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Koch, S. B.
Reed, J. C.

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Alleman, G.

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Parkinson, J. C.

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Schultz, L. C.

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Schleeder, L. B.

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Richards, E.

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Saunders, W. M.
Slade, W. C.

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Mills, J. E.

Sumter—
Van Deventer, H. R.
Zimmermann, J. G.

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Trojan—
Bowman, F. C.

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La Follette—
Foust, T. B.

Maryville—
Glasscock, B. L.
Parks, R. E.

Memphis—
Holtzendorff, P. W.

TEXAS

Austin—
Harper, H. W.
Schoch, E. P.

El Paso—
Silverman, R. B.

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Slater, W. A.

Prescott—
Bradley, D. H., Jr.

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Bingham—
Barnes, W. A.

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Smith, F. W.

Salt Lake City—
Bradford, R. H.
Emery, W. L.
Jennings, E. P.
Letchfield, F. T.
Lyon, D. A.
Merrill, J. F.
Ralston, O. C.

VERMONT

Northfield—
Howard, S. F.

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Charlottesville—
Weaver, W. D.

Holcomb's Rock—
Lee, H. R.

Norfolk—
Webb, L. W.

Port Norfolk—
Hamilton, E. H.

Richmond—
Walters, Jos.

University—
Dunnington, F. P.

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Metaline Falls—
Wenner, R. S.

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Crim, L. P.
Thomas, B.

Spokane—
Armstrong, L. K.
Keffer, Frederick

Tacoma—
Everette, W. E.

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Charleston—
Carrier, C. F., Jr.

Clarksburg—
Chorpening, G. B.

Glen Ferris—
Huffard, J. B.

Morgantown—
Clark, F. E.
Hite, B. H.

Weirton—
Rese, Wm. F.

WISCONSIN

Madison—
Bennett, E.
Burgess, C. F.
Hamister, V. C. H.
Kahlenberg, L.
Kowalke, O. L.
Richardson, L. T.
Schulte, W. B.
Storey, O. W.
Watts, O. P.

Marinette—
Lathrop, L. H.

Milwaukee—
Bovee, B. A.
Kremers, J. G.
Raeth, F. C.

WYOMING

Thermopolis—
Freeman, G. N.

CANADA.

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Fowler, S. S.

Trail—
Batchelder, J. K.

Vancouver—
Barwick, W. S.
Boesch, J. E
Hayward, R. F.
Kendall, G. R.
McIntosh, D.

MANITOBA

Winnipeg—
Armes, H. P.
Morden, G. W.

NOVA SCOTIA

New Glasgow—
Cantley, T.

Sydney—
Collins, F. L.

ONTARIO

Kingston—
Goodwin, L. F.
Goodwin, W. L.

Niagara Falls—
Hendrie, G. A.

St. Catharines—
Heitmann, E.

Thorold—
Brockbank, C. J.

Toronto—
Bain, J. W.
Barrows, W. S.
Boswell, W. O.
Burt-Gerrans, J. T.
Gaby, F. A.
Guess, G. A.
Irving, T. C., Jr.
Kaemmerer, J. A.
Kenrick, F. B.
Landau, Alfred
Loudon, T. R.
Miller, W. L.
Moffat, J. W.
Turner, F. M., Jr.
Williams, E. R.
Wurster, O. H.

Welland—
Carnegie, E.
Turnbull, R.

Windsor—
Henderson, E. G.

QUEBEC

Buckingham—
Hambley, F. J.

Choisy—
Grageroff, I.

La Tuque—
Hanson, H. H.

Montreal—
Hough, A.
Jacobs, F. A.
Medbury, C. F.
Pascoe, C. F.
Stansfield, A.

Ottawa—
Haanel, E.
Simpson, Louis
Smart, R. S.

Quebec—
McKee, G. M.

Shawinigan Falls—
Acton, E. H.
Higgins, W. A.
Witherspoon, R. A.

SASKATCHEWAN

Saskatoon—
MacLaurin, R. D.

MEXICO.

Aguascalientes—
Wilkins, E. M.

Pachuca—
Girdwood, K. A.

CUBA.

Isle of Pines—
Roberts, I. L.

Jovellanos—
Weber, E. G.

SOUTH AMERICA.

BRAZIL

Rio de Janeiro—
De Medeiros. T. S. V.
Guinle, Eduardo

S. Paulo—
De Souza. E.
Walmsley, W. N.

Villa Nova de Lima—
Hill, Stafford
Jones, H.
Wilder, F. L.

CHILE

Chuquicamata—
Merrill, M. W.
Page, Wm. K.

Rancagua—
Ward, A. T.

Santiago—
Diaz-Ossa. B.

PERU

Lima—
D'Ornellas, T. V.

AUSTRALASIA.

NEW SOUTH WALES

Broken Hill—
Gepp, H. W.

Cutana—
Du Faur, J. B.

Port Kembla—
White, E. A.

Moonta Mines—
Hancock, H. L.

Sydney—
Julius, G. A.
Murphy, R. K.

NEW ZEALAND

Christ Church—
Stark, E. E.

Dunedin—
Shepherd, F. R.

Epsom—
Gordon, H. A.

QUEENSLAND

Brisbane—
Henderson, J. B.
Jackson, A. G.

Mt. Morgan—
Johns, M. J.

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Melbourne—
Creagh, E. C.
Gillies, P. M.

TASMANIA

Queenstown—
Sticht, R. C.

ASIA.

CHINA

Han-Yang—
Yang, Cho
Lincheng—
Kwang, K. Y.
Shanghai—
Richardson, H. K.
Wen, C. Y.

INDIA

Bangalore—
Arunachela, T. K.
Kankanhalli—
Tate, J. V. E.

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Akitaken—
Kaneko, K.
Kobe—
Tachihara, Jin
Tada, S.
Kyoto—
Namba, M.
Nishikawa, Kikei
Yoshikawa, K.
Osaka—
Murahashi, S.
Noguchi, Jun
Tokyo—
Hoshina, T.
Iwai, K.
Katsura, B.
Kawamura, T.
Kishi, K.
Masujima, B.
Nohara, T.
Oshima, Y.
Yonezawa—
Yamasaki, J.

AFRICA.

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Budapest—
Pikler, A. H.
Treibach—
Fattinger, F.
Vienna—
Helfenstein, A.

BELGIUM

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Stoll, C. G.
Brussels—
Cito, C. C.
Solvay, A.
Jemeppe—
Queneau, A. L. J.
Mons—
Henault,O-Dony
Neerpelt—
Raeder, Bjorn

FRANCE

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Bourdon, P.
Paris—
deGeofroy, A.
Drake, F. E.
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Keller, C. A.
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Ostheimer, J. W.
Riva-Berni, A. de

GERMANY

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Haber, Fritz
Reichel, W.
Bonn—
Bucherer, A. H.
Charlottenburg—
Engelhardt, V.
Reissenegger, H
Clausthal—
Hoffmann, R.
Dresden—
Schrey, A.
Essen-Ruhr—
Goldschmidt, H.
Frankfurt—
De Neufville, R.
Hamburg—
Arnemann, P.
Wohlwill, H.
Hanau—
Heraeus, H.
Hanover—
Arnemann, C.
Hohenlohehuette—
Gelbach, E.
Karlsruhe—
Askenasy, P.
Leipzig—
Le Blanc, M.
Schall, C.
Linz—
Calberla, R.
Luebeck—
Draeger, A. B.
Nurnberg—
Forchheimer, P. J.
Schwerte—
Amberg, Richard

GREAT BRITAIN

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Essex (England)—
Ashcroft, E. A.
Irvine, (Scotland)—
Walker, J. W.

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Smith, A. T.

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Cornthwaite, Haydn
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Goldstein, P.
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ITALY

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Ligure—
Giolitti, F.

Milan—
Rossi, C.

Rome—
Catani, R.
Chiaraviglio, D.
Morani, F.

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Bergen—
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Collett, Ove
Goldschmidt, H.
Hiorth, A.
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Johansen, G. H.
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Söderberg, C. W.
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Torell, T. F.

Fredriksstad—
Moltkehansen, I. J.

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Odda—
Giersten, S.

Rjukan—
Bonnevie, H.

Stavanger—
Jacobsen, F.

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Styri, H.
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Chateau, P.

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SWEDEN

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Yngstrom, L.

Gottenburg—
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Gullspang—
Hedlund, M.
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Ludvika—
Groenwall, Assar

Mansbo—
Carlson, B.

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Tingberg, Otto

Trollhattan—
Berglund, E. S.
Olaussen, K. O. E.

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Lindberg, S. C.

Vesteras—
Edstrom, J. S.

Westervik—
Tillberg, E. W.

SWITZERLAND

Basel—
Fichter-Bernoulli, F.

Geneva—
Gandillon, A.
Guye, P. A.
Lacroix, H.

Turgi—
Landolt, H.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, at a Joint Session with the American Institute of Mining Engineers, September 17, 1915; Dr. L. D. Ricketts in the Chair.

ROASTING AND LEACHING CONCENTRATOR SLIMES TAILINGS

By Lawrence Addicks.

Through the courtesy of Dr. James Douglas I am permitted to give a summary of some of the results obtained in leaching slimes tailings in a series of experiments conducted under my direction at Douglas, Ariz., during the past year.

While the test run for which the data are given deals with a particular case, much of the work is general in its application and may therefore be of interest.

This work was done upon the ores of the Burro Mountain Copper Co. A description of the geology of the district will be found in the paper by R. E. Somers published in the May, 1915, *Bulletin of the American Institute of Mining Engineers.*

The mineral is pyrite and chalcocite very finely disseminated throughout the gangue, and a characteristic of all the ores is the large amount of alumina present.

A representative analysis of the particular ore under consideration would be about as follows:

Cu	2.35	percent
Fe	1.5	percent
Al_2O_3	13.0	percent
S	3.0	percent
CaO	0.5	percent
K_2O	4.0	percent
SiO_2	70.0	percent
Ag	0.05	oz. per ton
Au	None	

The leaching of the ore direct was early dismissed from consideration for the following reasons:

1. The ore would have to be quite finely crushed to liberate the mineral for leaching; concentrating after crushing would cost but a few cents a ton; a higher total recovery would result from leaching tailings rather than ore.

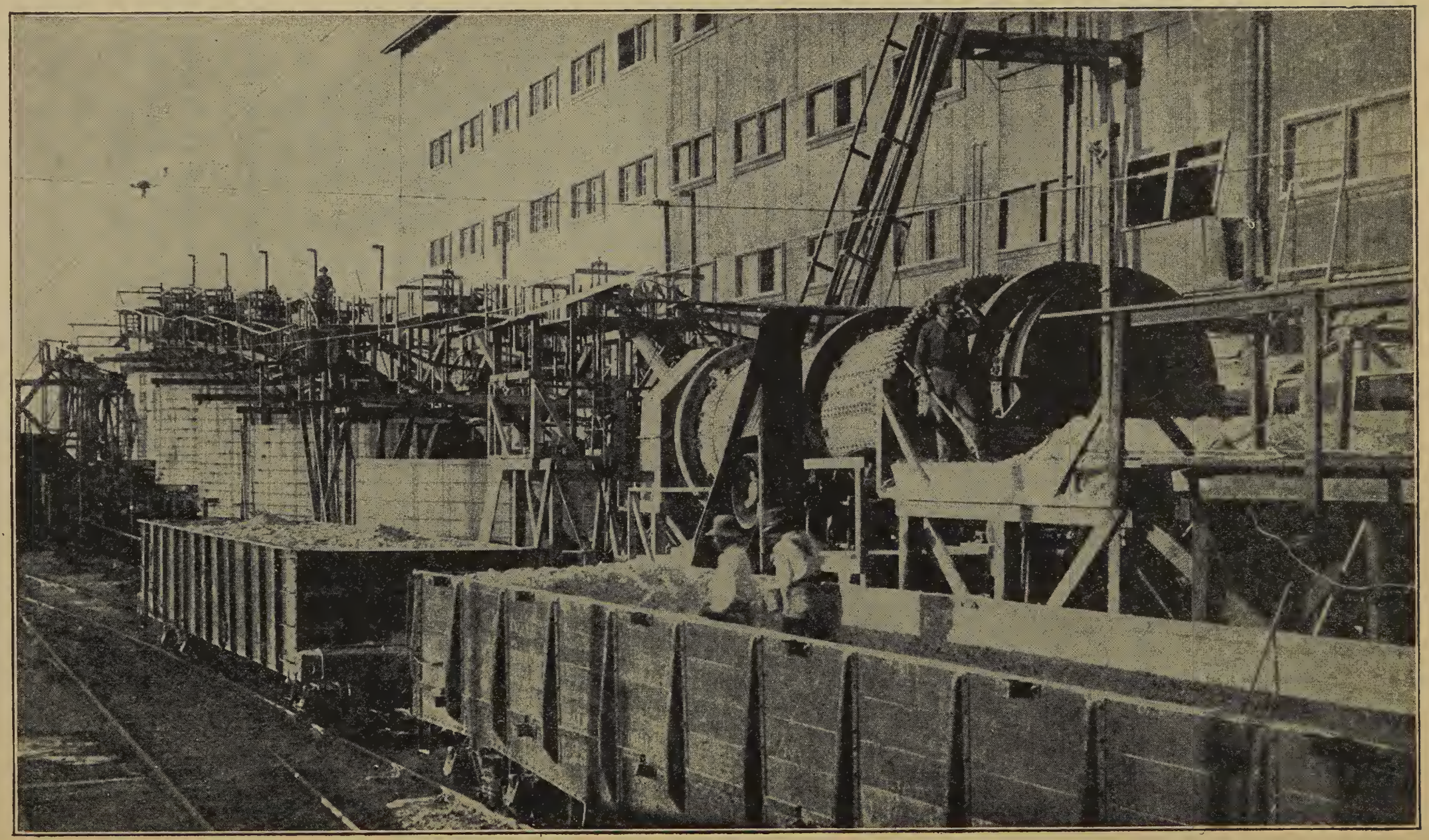


Fig. 1. General View of Leaching Plant.

2. Rough concentration would yield a suitable material for roasting to make sulphur dioxide or sulphuric acid in connection with the leaching scheme.

3. Such a program put the question of cost *vs.* recovery on a basis where flotation and discarding of tailings were directly comparable.

Concentrating experiments already available indicated that the tailings would consist of about 50 percent of sands running about 0.3 percent copper, and therefore too low to justify re-treatment, and about 50 percent of slimes running perhaps 1 percent copper, and it was on this latter material that the large-scale work was finally done.

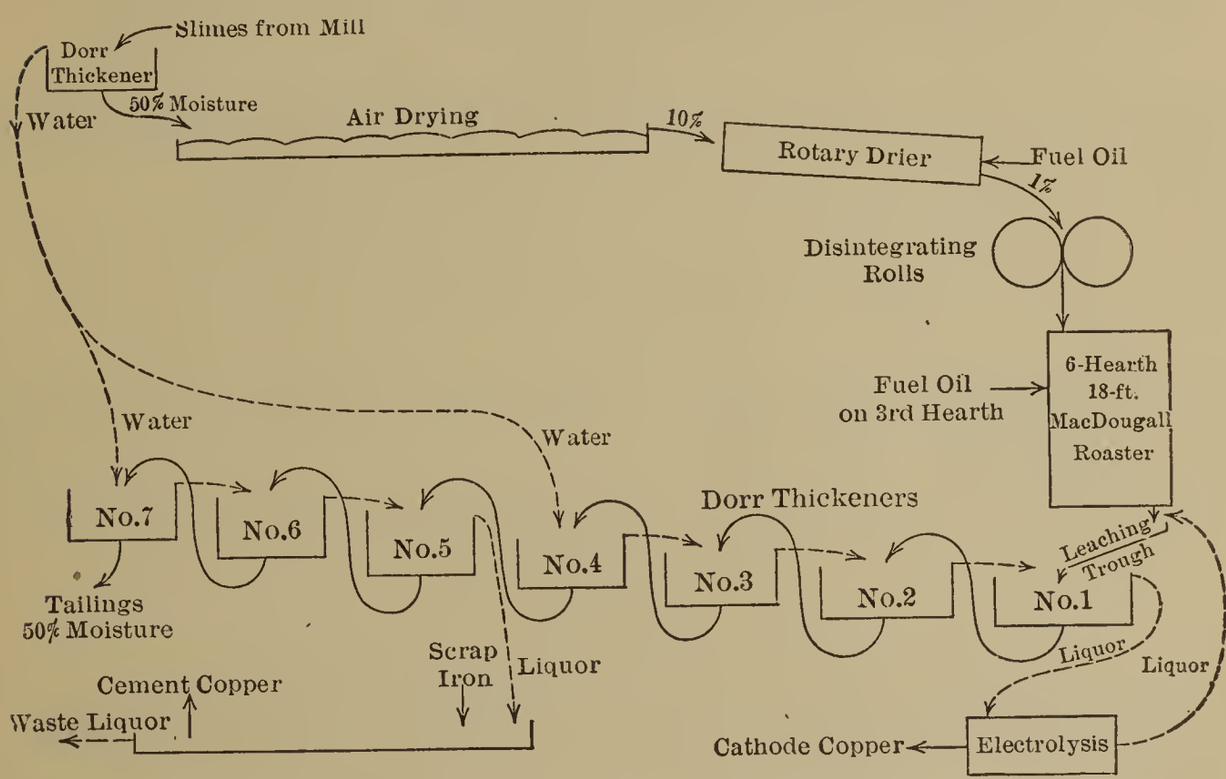


FIG. 2. Flow Sheet of Leaching Plant.

At first flotation gave very unsatisfactory results, due primarily to the readiness with which the fine mineral particles became coated with a film of oxide upon exposure while concentrating, but later developments in this field overcame these difficulties and it became apparent just about the time the leaching plant was being started that the concentrator recovery was going to be so high that re-treatment of the tailings would not be justified. Nevertheless, for the sake of the data it was decided to carry through a representative run, the results of which are discussed below.

Fig. 1 is a view of the leaching plant, and the general scheme is shown in the flow sheet, Fig. 2. As the development of the electrolytic precipitation is really a subject apart from the leaching of the slimes, the results from this part of the work have been reserved for a separate paper. A part of the copper is shown recovered as cement in order to give a means of holding the iron and alumina in the liquor to be electrolyzed down to the desired point. A high ratio of washing can be used in the thickeners delivering to the cementation launder; in the remaining thickeners the ratio is governed by the evaporation loss, as there is no other outlet for liquor.

The experiments will be taken up in detail under the headings of: (1) drying, (2) roasting, (3) leaching, and (4) washing.

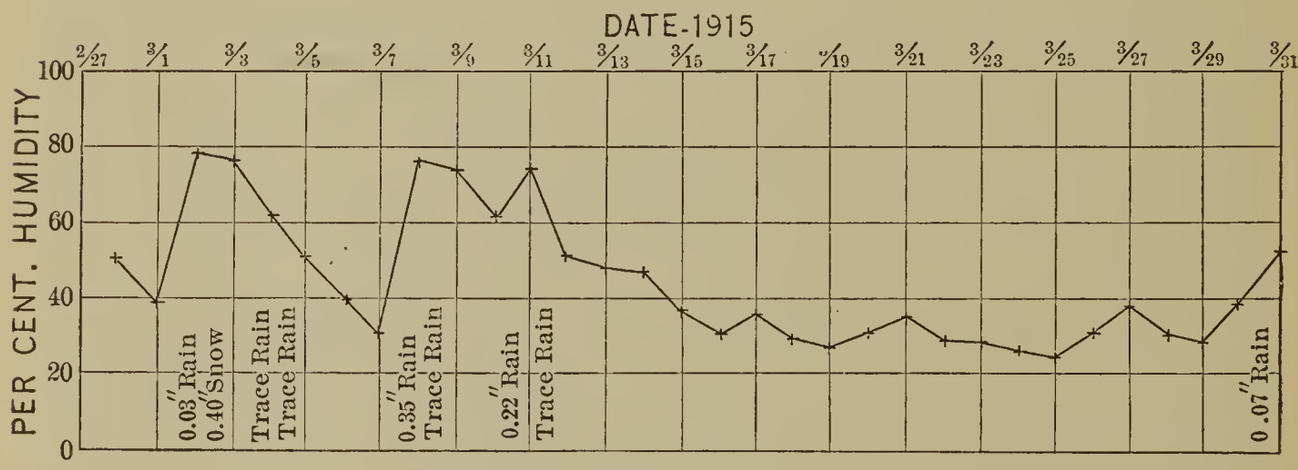


FIG. 3. Moisture in Air.

Drying.

As the slimes would be delivered from the concentrator in suspension as a thin pulp it became necessary to consider carefully the question of drying.

Thickening experiments indicated that there was a critical degree of moisture of about 45 percent, below which pumping the settled slimes resulted in further classification of the fine particles instead of delivering average pulp, so that thickening in a standard Dorr unit to 50 percent of moisture was established as the first step.

As fuel is very expensive at the location in question and no waste heat can be counted on except that from the roaster gases, experiments were made with drying by exposure to the desert sun and winds. The heavy pulp could be poured into a shallow

basin and the more or less dried slime reclaimed by some mechanical method for much less expense than an equivalent drying using artificial heat would cost. It was found that the pulp settled to about 30 percent of moisture very readily when allowed to drain and that reasonably dry material could be obtained by a month's standing.

Figs. 3, 4, 5, and 6 give the measurements taken during the trial on three test beds, 10 ft. (3 m.) square and respectively 2, 6, and 10 in. (5, 15, 25 cm.) deep, which were exposed to the atmosphere for about a month.

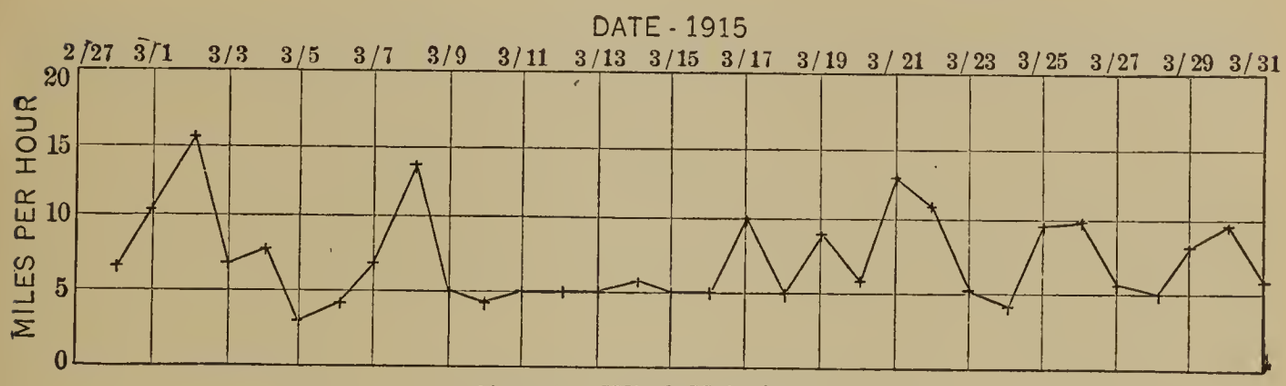


FIG. 4. Wind Velocity.

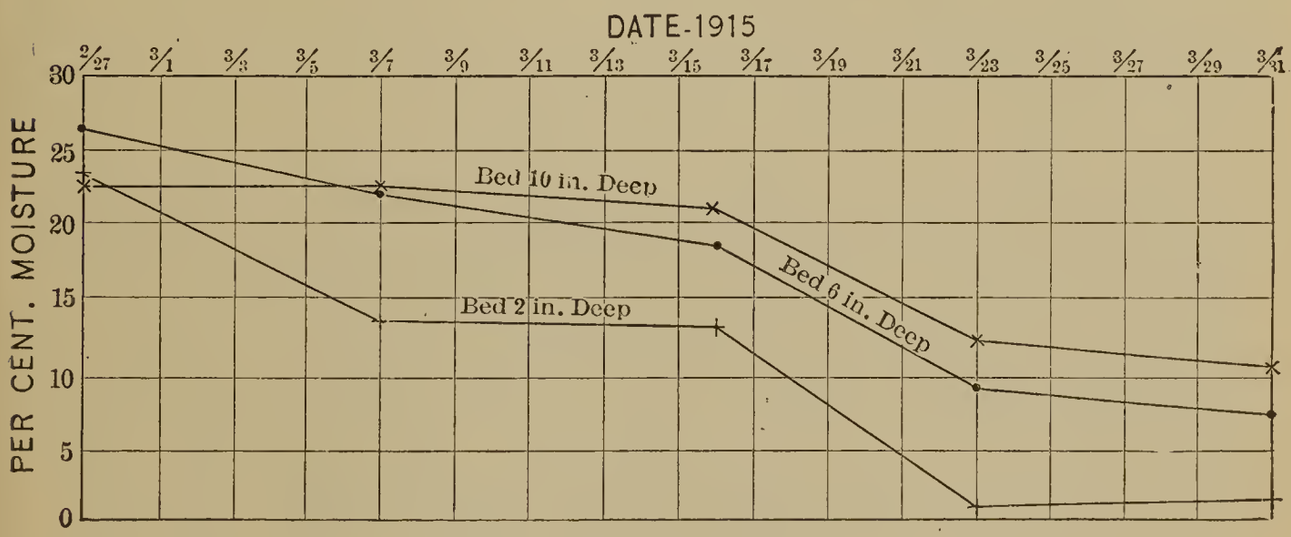


FIG. 5. Moisture in Slimes.

The climatic conditions are shown in Figs. 3, 4, and 6 and it will be noted that periods of both cold and wet weather were encountered during the first part of the run, much more favorable conditions following in the last two weeks. A bed only 2 in. (5 cm.) deep would cost a good deal to reclaim, but the rate of drying, as shown in Fig. 5, was thought to indicate that a reasonably thick bed could be brought down to 10 percent of

moisture without an excessive period of standing, and it seems probable that this will be the cheapest way to obtain this preliminary drying.

Up to this point the experiments were conducted on relatively small quantities of material, but starting with the following step —drying in the rotary kiln—large tonnages were handled. Instead of using atmospheric drying before feeding to the kiln, steam coils were buried in the cars of mushy slimes shipped to the experimental plant, bringing the moisture down to about 25 percent, when it was shoveled directly to the drier.

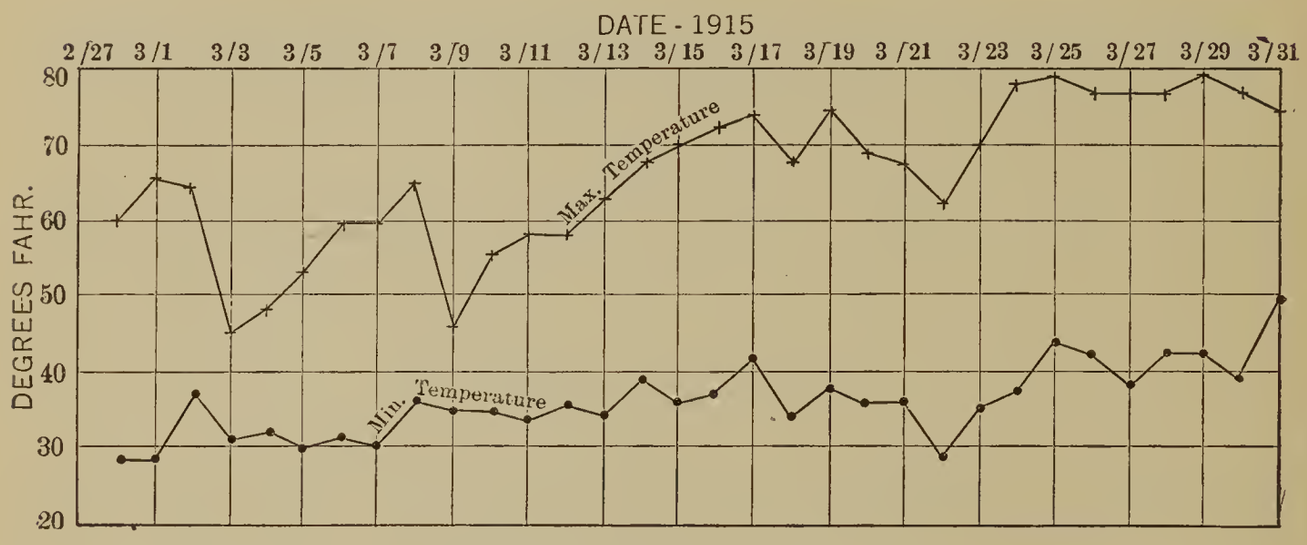


FIG. 6. Temperature of Air.

This drier was one of the old Douglas roasters, 7 ft. (2.1 m.) in diameter and 31 ft. (9.3 m.) long. It was used as an ordinary unlined rotary kiln, with channel-iron spilling blades throughout the first two-thirds of its length and cast-iron balls 3 in. (7.5 cm.) in diameter feeding against a delivery screen made of sheet-iron plate with 1½-in. (4 cm.) round holes. The idea was to dry and pulverize any caked nodules in the one apparatus. The outside was lagged with 1½-in. (4 cm.) magnesia block, and heat was supplied by three oil burners at the delivery end. Two typical runs gave the following results:

Days run	23.0	12.0
Total tons dried	710.0	388.0
Tons per day	30.9	32.3
Percent moisture, entering	26.6	10.0
Percent moisture, leaving	1.1	2.0
Gallons fuel oil per day	404.0 (1521 liters)	154.0 (583 liters)
Gal. fuel oil per ton dried	13.1 (49.6 liters)	4.8 (18.2 liters)

In general, it was concluded that about ½ gal. (1.9 liters) of fuel oil must be provided for each unit of moisture in the ore to be dried, so that 5 gal. (19 liters) would have to be charged against drying a 10 percent product from the atmospheric drying beds, although this amount might be lowered in a properly designed drier. The capacity of the drier was too low for the roaster used and the pulverizing action of the iron balls inadequate, so the dried material was passed through a pair of dis-

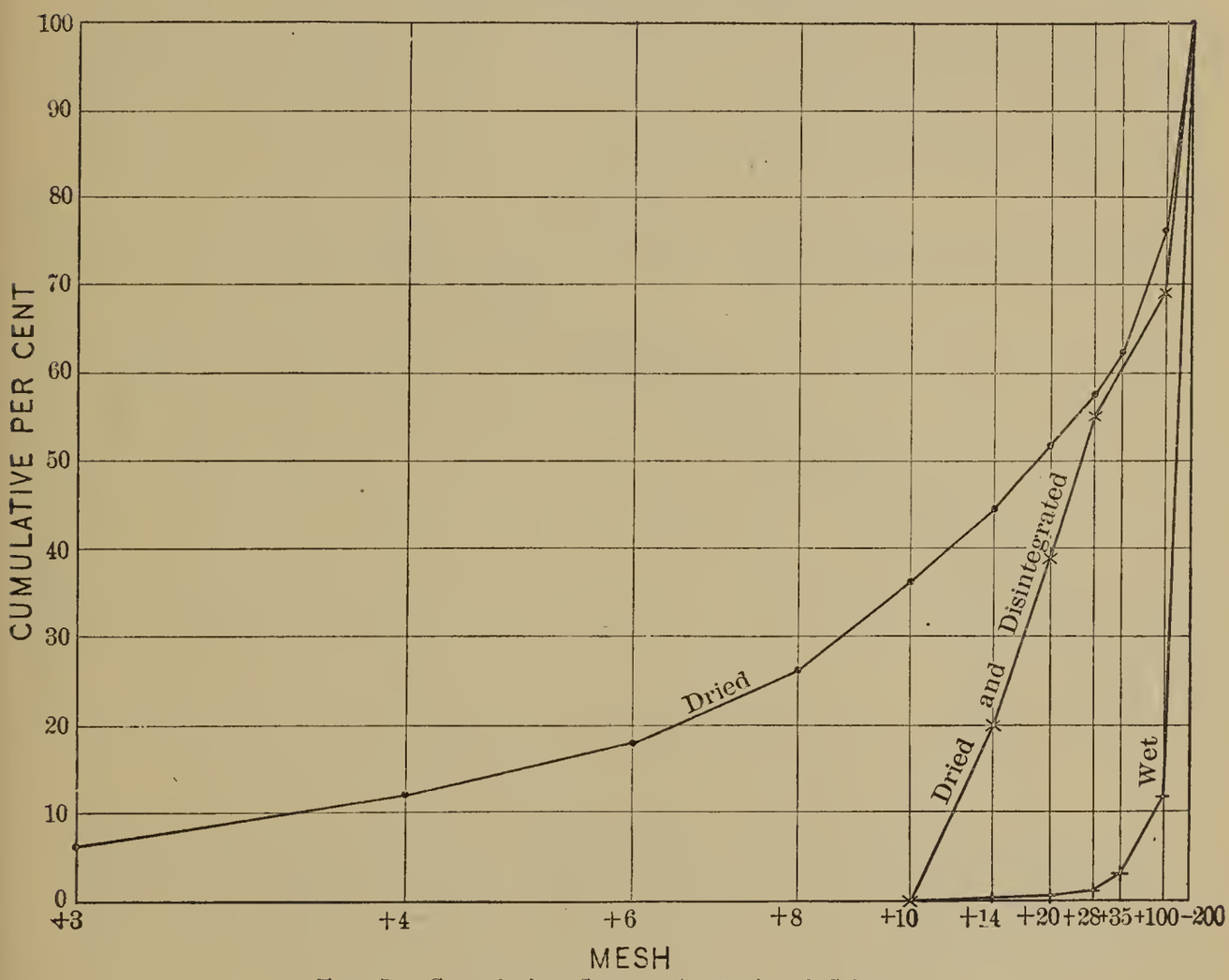


Fig. 7. Cumulative Screen Analysis of Slimes.

integrating rolls, returning any oversize through a 10-mesh screen, and dried and disintegrated material was stored ahead of the roaster.

Fig. 7 shows cumulative screen analyses of the original wet slimes, the drier product, and the disintegrated material, made on the usual Tyler direct diagram. It must be remembered that the lumps formed in the kiln could be readily crushed between the thumb and forefinger, being merely caked clay. The danger

was that these lumps would be burned hard in the subsequent roasting.

The arrangement of the drier with skip feeding to roaster, and the row of Dorr thickeners, can be readily seen in Fig. 1.

Roasting.

The roasting was carried out in a standard six-hearth, 18-ft. (5.4 m.) MacDougall furnace with water-cooled arms, fuel oil being introduced on the third hearth. No change was made in the furnace for this work except to replace parts of the upper brickwork with firebrick. Fig. 8 shows the tonnage fed to the furnace daily during the particular run with which the remainder

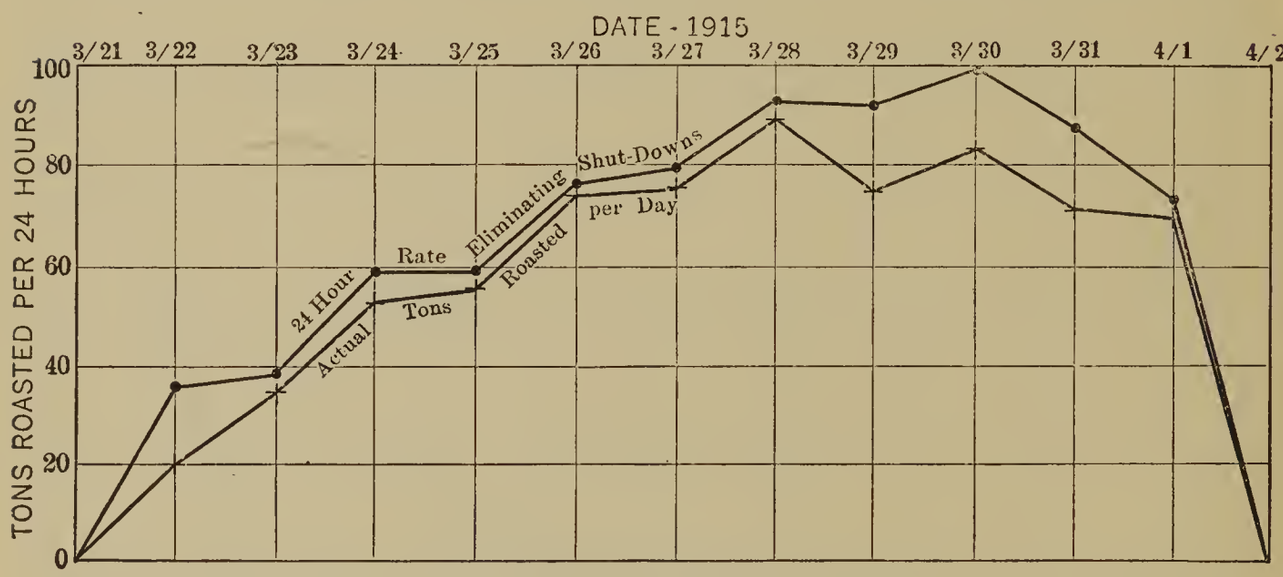


Fig. 8. Tons Ore to Roaster.

of this paper chiefly deals. When the arms began to be buried the speed of rotation was increased from one revolution in 69 sec. to one in 60 sec. No trouble was experienced in the operation of the furnace.

Fig. 9 shows how the fuel-oil consumption was gradually cut down as the size of charge was increased. It is evident that 100 tons a day can be roasted with about 3.5 gal. (12.8 liters) of fuel oil per ton. The fuel oil burned was regulated so as to keep the maximum temperature on any hearth at about 950° F. (510° C.). Previous small-scale experiments had indicated that the proper roasting range lay between 900° and 1,100° F. (483°-596° C.). Fig. 10 shows a log of the daily temperatures on the second, third, fourth, and fifth hearths. It will be noted

that the heat zone descended in the furnace as the tonnage increased. This is shown diagramatically in Fig. 11. At the same time the efficiency of the roast increased, as shown by Fig. 12. This is apparently due to the fact that at the higher rates roasting temperatures were obtained on the fourth and fifth hearths, which were free from the more or less reducing atmosphere of the third and higher hearths due to the fuel oil.

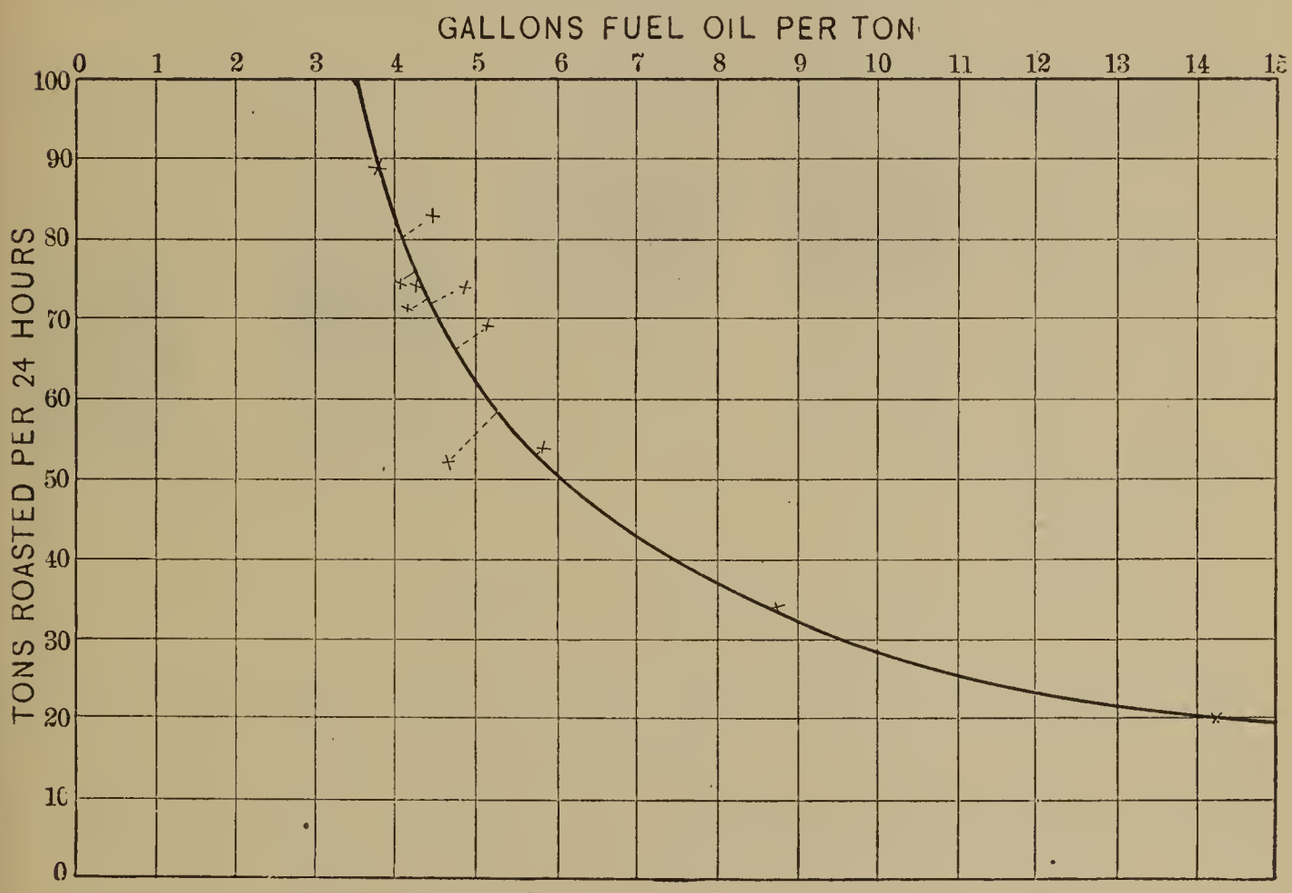


FIG. 9. Roaster Tonnage *vs.* Fuel-Oil Consumption.

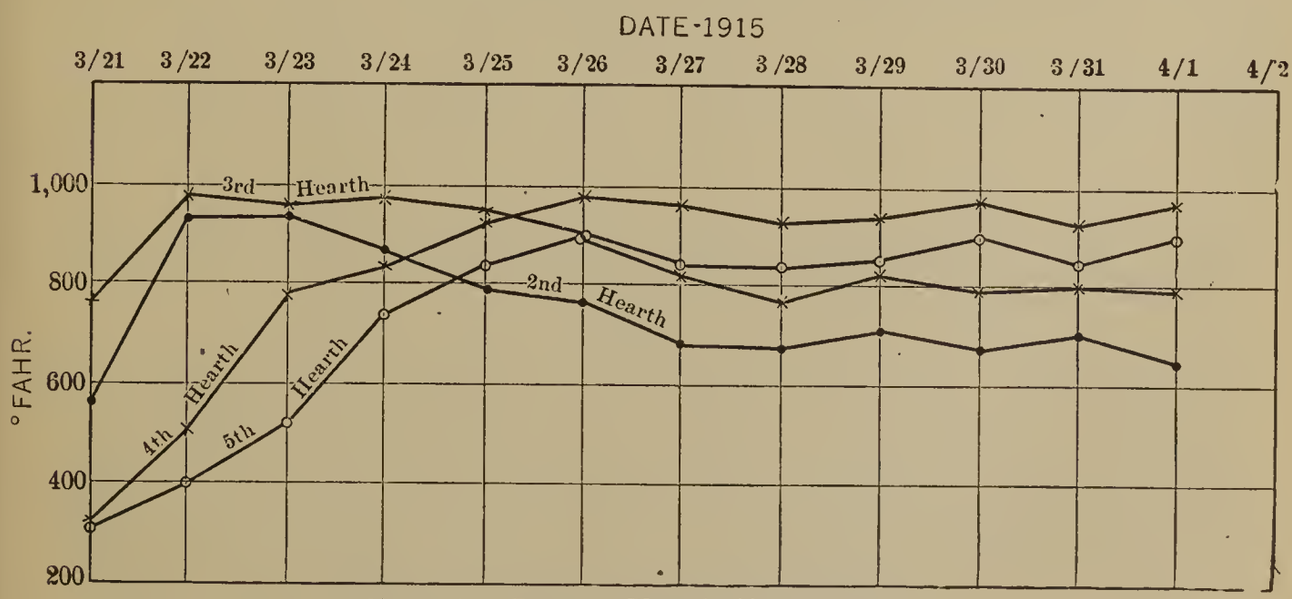


FIG. 10. Roaster Hearth Temperatures.

Leaching.

The hot calcines from the roaster were delivered through a spout casting made of Duriron into a triangular trough about 30 ft. (9 m.) long sloping 1¼ in. (3.2 cm.) to the foot, which delivered directly into the first of the series of Dorr thickeners used

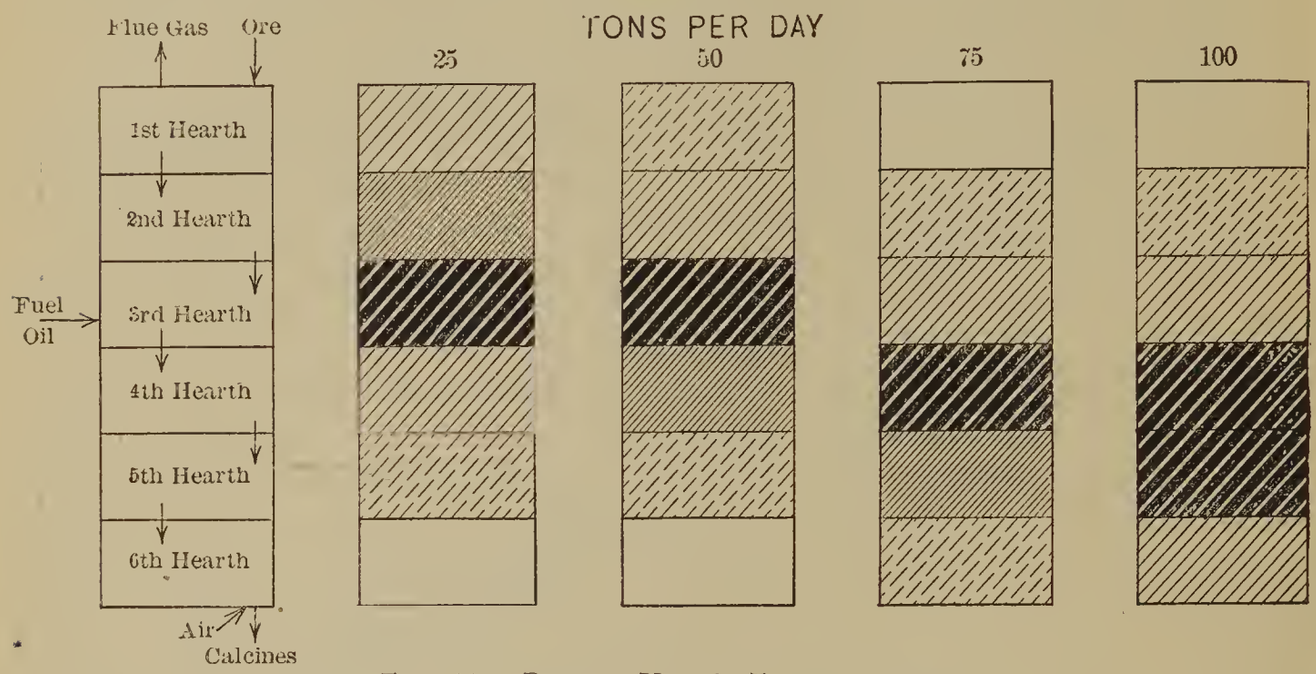


FIG. 11. Roaster Hearth Temperatures.

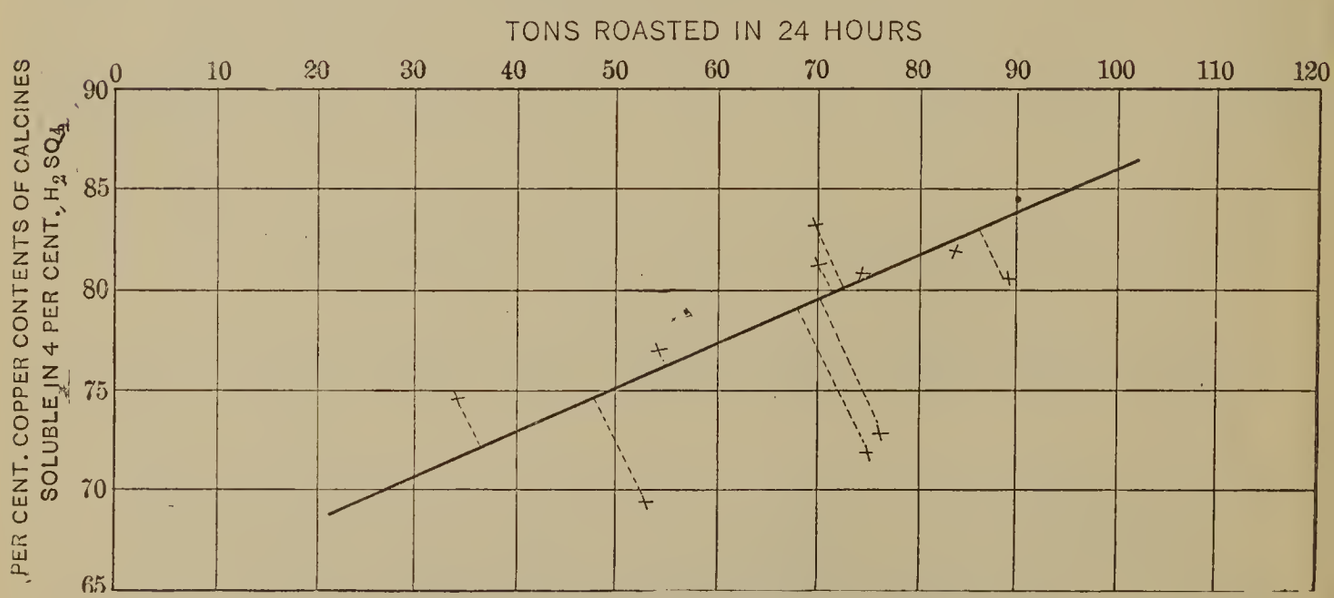


FIG. 12. Variation of Roaster Efficiency with Tonnage.

for washing. This trough served three purposes: (1) that of leaching by agitation; (2) that of mechanically conveying the calcines from the roaster to the washing apparatus; and (3) that of absorbing the sensible heat of the calcines, thereby furnishing a warm liquor for electrolysis. A similar arrangement is de-

scribed as doing excellent work in another field, by Hofmann in his *Hydrometallurgy of Silver.* A deep triangular trough was first constructed of common lumber. This was then lined with sheet lead to make it liquor proof. Inside the lead lining boards were loosely laid to prevent mechanical erosion of the lead by the calcines. A flat wooden cover was laid on top of the launder to keep down the steam and dust. This latter was not

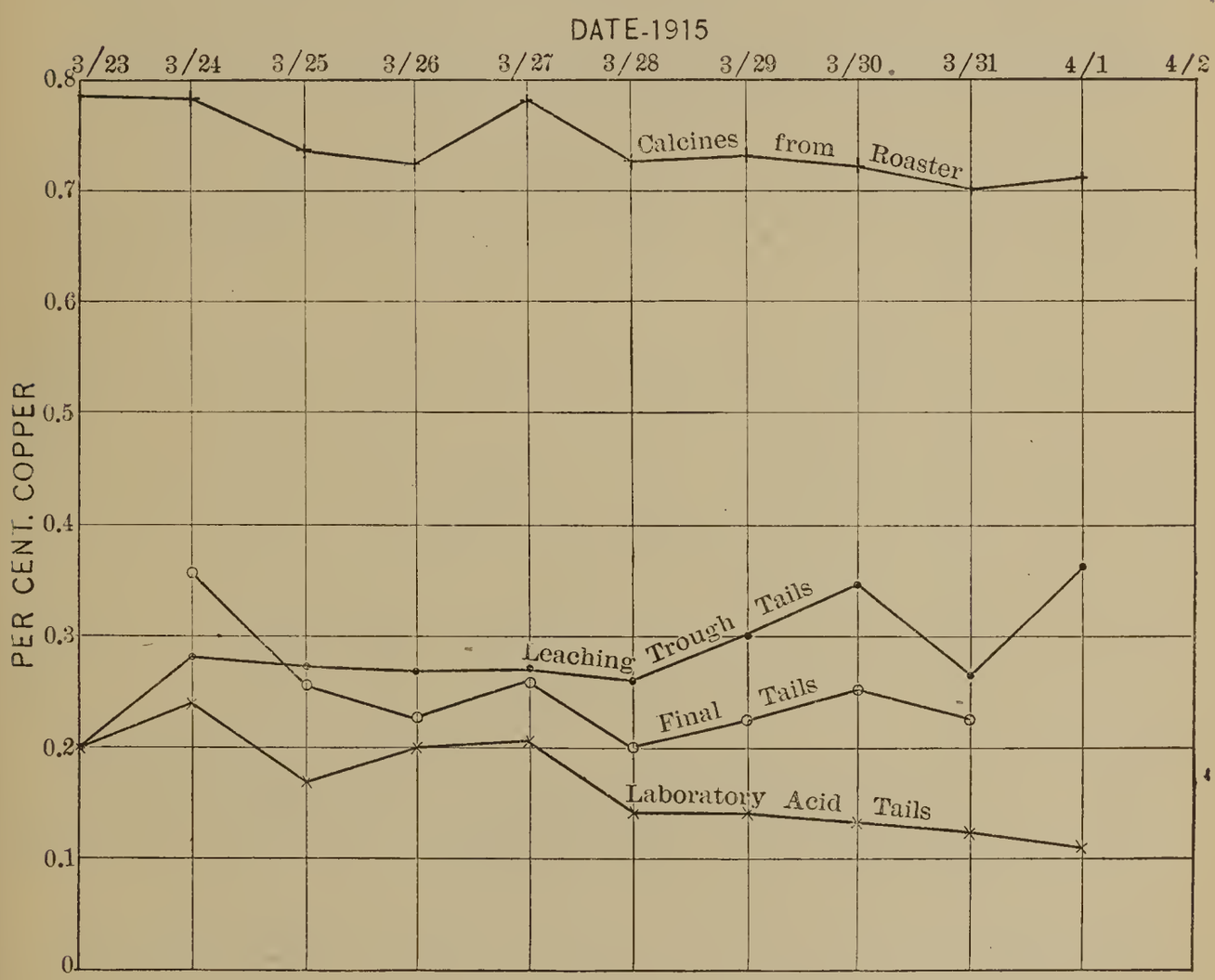


FIG. 13. Copper Contents of Tailings.

excessive, and would have been very slight had a more even delivery of calcines been made at the head of the sluice. The furnace arms alternated with light and heavy charges through the bottom drop hole and these were spread out over a reasonable time interval by placing an adjustable gate in the delivery spout, something on the plan of the classic hour glass. This worked fairly well, but it would have been better to have arranged some extra arms on the bottom hearth.

The copper content of the tailings at various points in their travel through the plant is shown in Fig. 13. The free sulphuric acid content of the liquor is shown in Fig. 14 and the effect of this strength of acid upon total extraction in Fig. 15.

The slimes as received assayed 0.84 percent copper. Fig. 13 shows that the calcines averaged about 0.74 percent copper, the grade falling as the furnace was gradually speeded up. This difference in assay was carefully investigated in the laboratory and it seems very improbable that it was due to the formation of insoluble copper compounds during the roast, as three acids

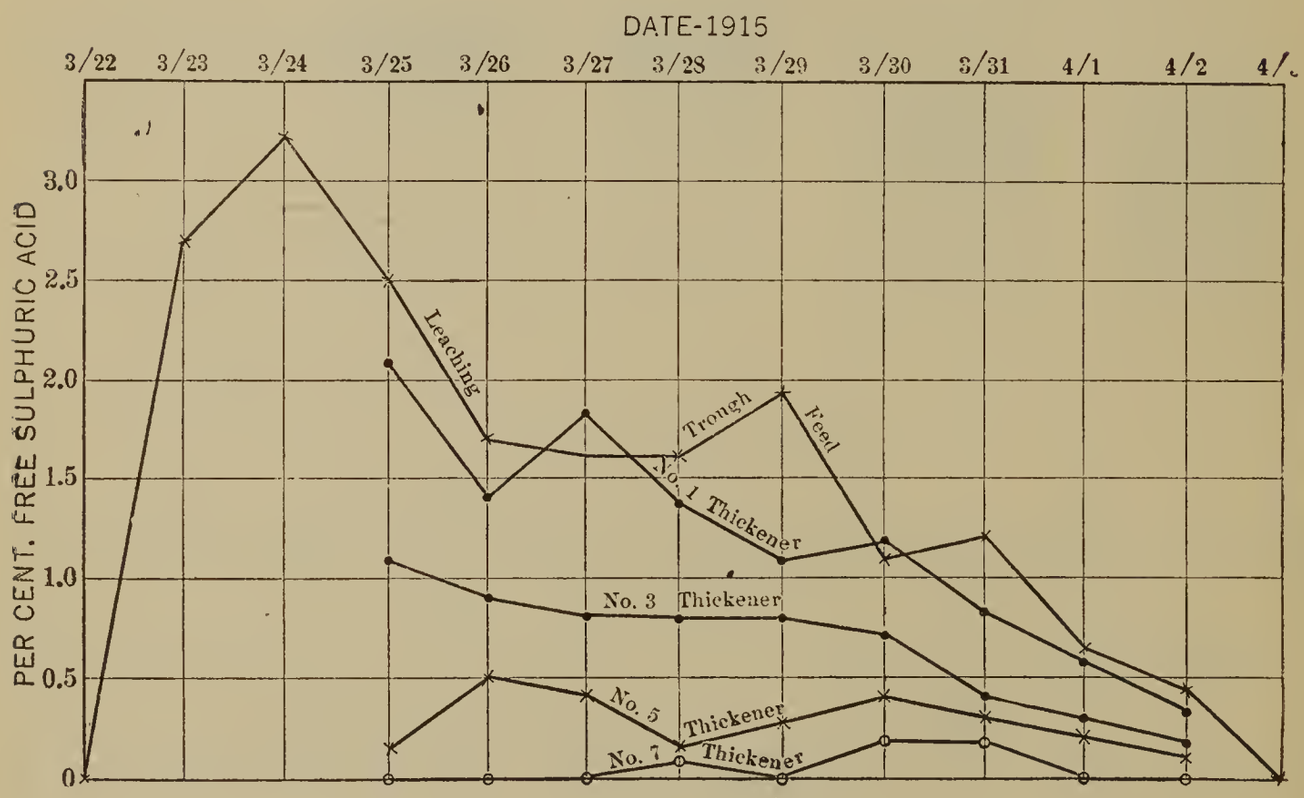


Fig. 14. Acid in Liquors.

were used in the assay and various methods yielded but the merest traces of copper from the assay residue. The most probable explanation lies in the formation of particles of anhydrous copper sulphate during the roast, which blew over with the flue dust. No measurements were made of the flue dust, as the furnace discharged into a common flue with other roasters treating concentrates.

The tails, as determined in the laboratory by heating samples of the calcines in 4 percent sulphuric acid, showed 0.2 percent copper, gradually dropping to 0.1 percent as the furnace efficiency increased with the load. The actual final tails discharged from

the last thickener ran about 0.1 percent higher than the laboratory-leached calcines and laboratory test showed this 0.1 percent to be present as soluble copper. This same margin has been noted by Croasdale in his paper presented last year on his experiments at Ajo, and he there attributes it to the impossibility in practice of washing ore free from soluble salts. Fig. 15, however, seems to indicate that the difference in this case is largely due to the stronger acid liquor used in the laboratory tests.

Fig. 14 shows that the run was started with over 3 percent of free sulphuric acid at the leaching trough and that this strength was allowed to exhaust itself gradually upon the entering ore as

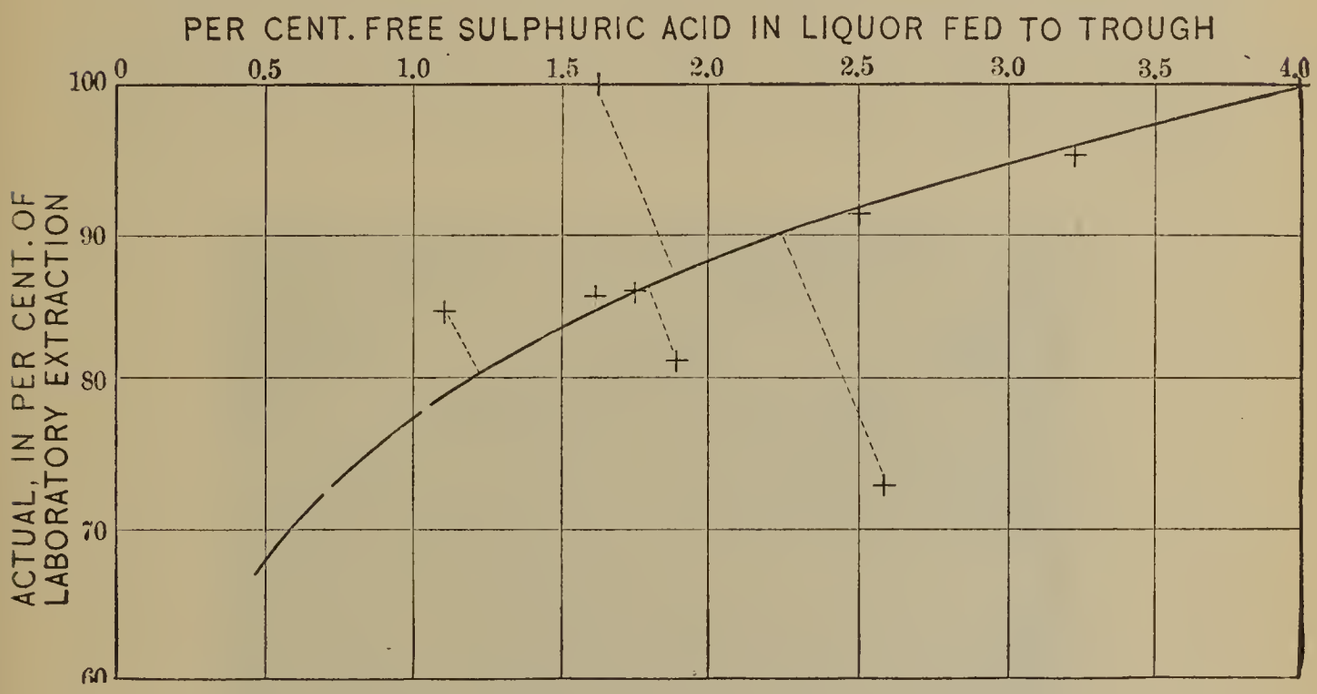


Fig. 15. Free Acid in Liquor *vs.* Efficiency of Extraction.

the run proceeded, the difference between final actual tails and laboratory tails increasing as the acid dropped. This same ratio is the basis of Fig. 14. It seems probable, therefore, that the strength of acid used will have to be considered in its bearing upon efficiency of extraction.

The leaching trough discharge ran but a few hundredths of a percent higher in copper than the final tails after seven washings, showing that over 90 percent of the leaching was done in the few seconds taken to travel down the trough. This high efficiency is due to the violent agitation when the hot calcines meet the relatively cool liquor, and to the fact that each particle of solid meets a fresh entering drop of liquor at the head of the

trough, obtaining the full efficiency of the acid strength. An actual over-all extraction in practice somewhere in the seventies seems assured from these experiments.

Washing.

The separation of the dissolved values from the exhausted slimes was one of the main problems presented. Any method of percolation was out of the question owing to the extremely fine state of subdivision of the material. The acid liquors employed similarly ruled out many of the mechanical filters. It was finally decided to try out continuous countercurrent decantation with Dorr thickeners of the acid-proof type of construction, some experience with which had been gained at the installation at the Butte-Duluth Mining Co.'s plant. Two 30 by 10 ft. (9 x 3 m.) and five 24 by 10 ft. (7.2 x 3 m.) tanks with suitable

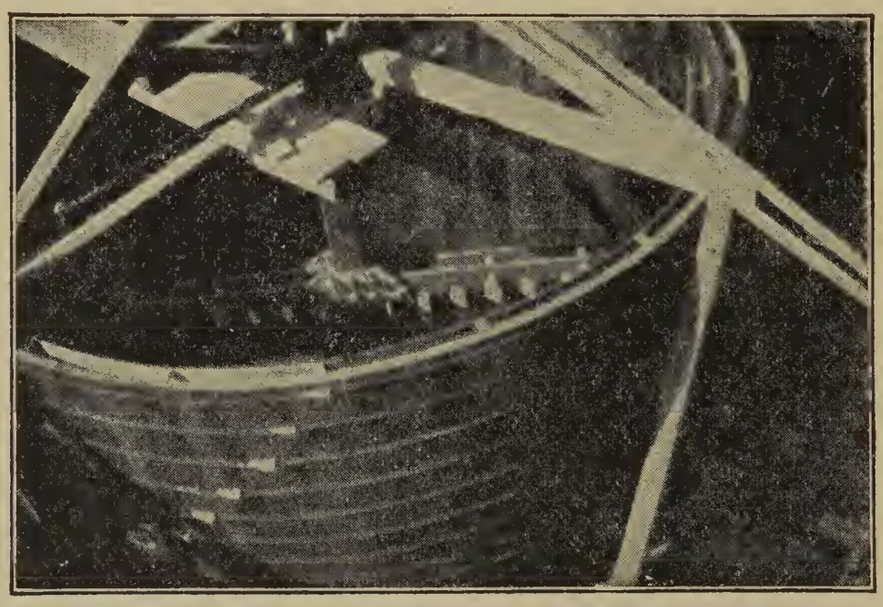


Fig. 16. Thickener Paddle.

mechanisms and wood-stave pipes and fittings for 4-in. (10 cm.) air lifts were therefore ordered and connected after erection in accordance with the flow sheet shown in Fig. 2.

The acid proofing of these mechanisms consisted of the substitution of wood for iron in the under-liquor parts. In turn, this called for some changes in design, two arms being used in place of four and the inclination of the swept floor being lessened. Both these changes increased the digging load and the arms tended to ride rather than dig, extreme cases overstraining the

unit. In spite of these difficulties the thickeners proved a practical apparatus. I believe, however, that the original metal construction properly protected by lead and equipped with Duriron rakes would be an improvement. An idea of the wooden construction can be obtained from Fig. 16.

The main difficulty was with the air lifts and I am satisfied that these are not practical for the particular case. It must be remembered that it was desired to make an underflow of 50 percent solids and that in the first thickeners many small lumps of slime had to be handled. When an air lift was gradually throttled until the desired thickness was obtained it no longer acted as a pump but more like a cannon, and a small capacity was obtained, finally resulting in one of two undesirable climaxes: Either a few small lumps settled out in the horizontal pipe under the tank, due to the slow flow, thereby choking it, or the lift would run thin for a moment followed by a rush as the normal pumping action was restored, stirring up the settled slimes and requiring constant attention for the next half hour in order to get the desired thickness of underflow. Also, the scouring action on the wood elbow at the point where the air was introduced was excessive, pipes sometimes wearing through in 24 hr.

Simple spigot discharge into a launder with some mechanical means of elevating was not promising, again due to obstructions making the flow of such a thick pulp very hard to regulate. Finally upon Mr. Dorr's suggestion two changes were made: (1) a diaphragm pump was tried, and (2) the remaining air lifts were arranged to return a part of the underflow to the same tank, thereby increasing the solids moved and keeping the rate of flow in the horizontal feed pipe above the critical speed at which lumps settled out.

The diaphragm pump was an entire success. In the first place, the delivery depends almost entirely upon the stroke and speed and is not influenced by a momentary change in thickness as in the case of the air lift. Then the suction has the entire pressure of the atmosphere at its command and this is exerted whenever an obstruction is encountered. In fact, an ore sack and a pair of gloves were pumped up, to the surprise of the operator. It is astonishing how many things find their way into a system of this kind. A watch and fob and a brace and bit were among the

articles added to our museum. Finally, the solids are moved steadily along and the scouring action is reduced to a degree which seems to make the use of wood pipe and fittings entirely practical. The pump was an ordinary 4-in. (10 cm.) Gould contractor's pump with cast-iron body. The metal parts could readily be made of Duriron or other acid-resisting material.

During the run the temperature of the liquor in the first thickener gradually rose from 56° F. (13° C.) at the start until 100° F. (38° C.) was reached on the sixth day, at which point it was maintained by the sensible heat of the entering calcines. It was found possible to settle as high as 125 tons of solids in 24 hr. in one of the 30-ft. (9 m.) tanks. The overflow by actual test showed but 3 lb. (1.4 kg.) of solids to the ton of liquor.

The liquors during the run accumulated sulphates corresponding to 10.0 lb. (4.5 kg.) copper, 4.3 lb. (2.0 kg.) iron, and 16.2 lb. (7.4 kg.) alumina per ton of slimes leached. The actual acid consumed was 49.0 lb. (22.2 kg.). The acid equivalent of the corresponding metallic oxides is 70.5 lb. (32.0 kg.) showing the presence of considerable sulphates in the calcines. A laboratory test on the calcines, using 4 percent acid, showed a consumption of 68.9 lb. (31.3 kg.) and a similar test on the product of a small-scale roast 69.1 lb. (31.4 kg.) acid per ton. It appears, therefore, that less acid will be used in practice than in laboratory tests. Unfortunately, the run was not sufficiently prolonged to determine whether the proportion of impurities dissolved decreased as the liquors became more concentrated.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, at a Joint Session with the American Institute of Mining Engineers, September 17, 1915, Dr. L. D. Ricketts in the Chair.

THE ELECTROLYSIS OF COPPER SULPHATE LIQUORS, USING CARBON ANODES.

By Lawrence Addicks.

Through the courtesy of Dr. James Douglas, I am permitted to give the results of quite an extended research conducted at Douglas, Arizona, on the possibilities of electrolytic recovery of copper from liquors resulting from sulphate leaching.

Starting with sulphide copper ores or concentrator products therefrom, which was the particular case under consideration, the simplest form of the proposition is to make sulphuric acid from concentrates by the usual roasting procedure, use this for leaching, electrolyze with lead anodes and precipitate upon iron sufficient of the liquor to maintain a reasonable degree of purity in the electrolyte. Such a method is commercial when there is no serious competition by other processes, as where concentrator tailings are very rich in values or where some local handicap to smelting exists, or where there is a profitable market for a surplus of sulphuric acid.

A very different way of attacking the problem was the old Siemens-Halske process, where ferric sulphate was used for the direct consumption of sulphides, the resulting ferrous-cupric sulphate liquor being electrolyzed in a diaphragm cell, obtaining a copper cathode and regenerating the ferric sulphate at the same time. This failed, partly due to the non-existence of a satisfactory diaphragm and partly to the shortcomings of the leaching agent.

Then Tossizza attacked the question by applying the long known action of sulphur dioxide gas as a depolarizer, introducing it directly into the cell, making sulphuric acid in accordance with the inclusive reaction,

$$CuSO_4 + SO_2 + 2H_2O + \text{current} = Cu + 2H_2SO_4$$

and reducing the voltage in proportion to the energy of oxidation at the anode. The direct use of sulphur dioxide as a depolarizer is undesirable for three reasons: (1) the escaping gas makes the atmosphere of the cell room unbearable and the ventilating problem, while perhaps not insurmountable, would be a very serious matter; (2) the gas escapes so readily from a warm liquor in motion that the consumption would be prodigal and there are limits, even though rather liberal ones, upon the quantity available; (3) it is a difficult matter to obtain a sufficient absorption for efficient depolarization, using roaster gas, unless compressors or other complications are resorted to.

The research work finally developed a process based upon the depolarizing value of ferrous sulphate, using a carbon anode, the sedative value of aluminum sulphate (U. S. Patent No. 1,138,921) thereby restraining the redissolving of the cathode copper, and the reduction of the ferric sulphate by sulphur dioxide outside of the cell room. It is the purpose of this paper to discuss the various factors involved in this scheme of procedure.

While it is not possible to divorce entirely these different factors, for clearness' sake they will be taken up individually as follows:

(1) Circulation and Agitation.
(2) Anodes and Depolarization.
(3) Cathodes and Corrosion.
(4) Sulphur Dioxide and Reduction of Ferric Sulphate.
(5) Efficiencies.

CIRCULATION AND AGITATION.

In any electrolytic process the constituents of the electrolyte taking part in the oxidation at the anode and the corresponding reduction at the cathode must be continually supplied at the electrodes by some method of circulation at a rate sufficient to satisfy the demands of the current at the density employed. If this is not done the voltage will rise until the next reaction in line occurs, or if the voltage is limited, the current will fall, or flow spasmodically. In our particular case ferrous sulphate must be supplied at the anode fast enough to take up the oxygen released and copper at the cathode in sufficient quantity to prevent the liberation of hydrogen or precipitation of impurities. A

relatively low rate of circulation suffices at the cathode if the liquor is reasonably rich in copper sulphate, as demonstrated in ordinary refining with a soluble anode. At the anode, on the other hand, a violent circulation is necessary, and this is best obtained by agitation with compressed air, apart from the relatively low circulation necessary for replenishment.

The reason for this behavior of the anode is doubtless due to the fact that a gas is liberated on a rather rough surface and more or less of a mechanical scouring action is necessary as well as a sufficient concentration of ferrous iron. In ordinary refining work the liquor is circulated at a rate which displaces

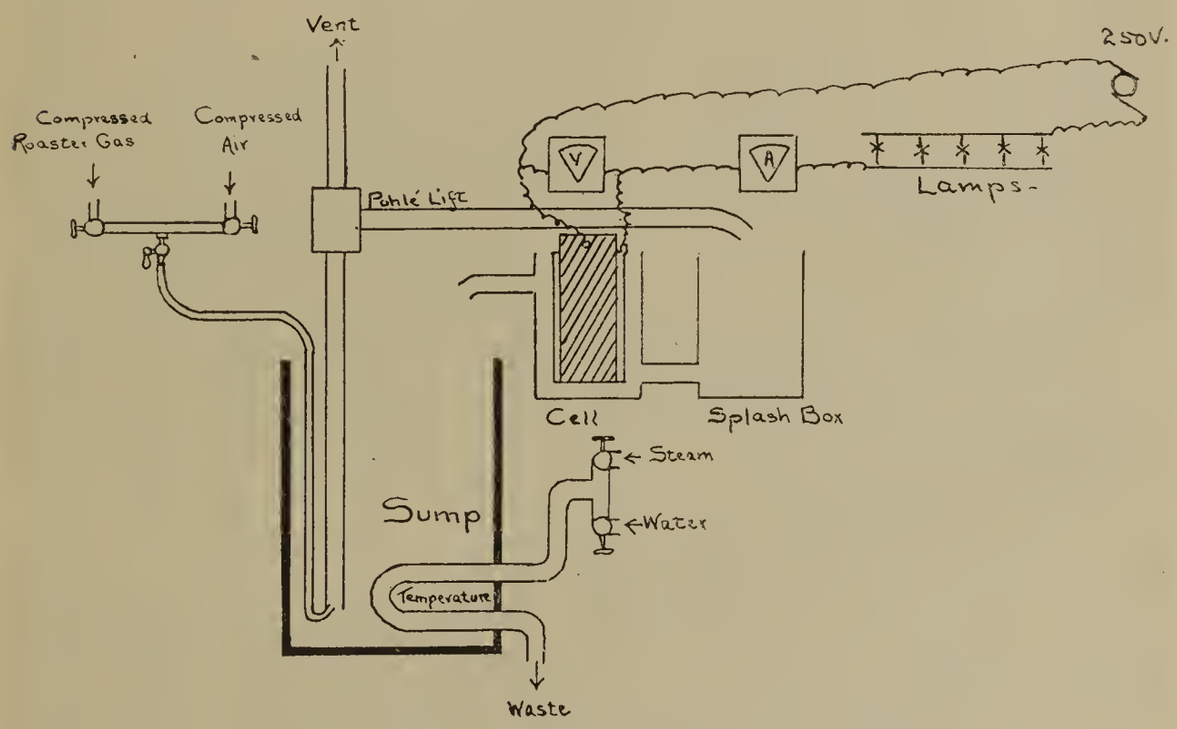


FIG. 1. Cell Arrangement for Voltage Tests.
Carbon Anode 3½ x 4 inches (9 x 10 cm.)
Copper Cathode 4 x 4 inches (10 x 10 cm.)
Electrodes 1 inch apart (2.5 cm.)

the contents of a cell in several hours. In this work, at a current density of 4 amperes per square foot (44 per sq. m.) a relatively low rate of circulation proved adequate, but at 8 amperes per square foot (88 per sq. m.) the contents of the cell, in small scale experiments, had to be displaced every 30 seconds, and at 16 amperes every 20 seconds, in order to obtain voltages indicating satisfactory depolarization, although these were readily reached by stirring or agitation. Any method of agitation which affords rapid movement of the electrolyte over the face of the anode may be used, but the introduction of compressed air at

the bottom of the cell seemed the most practical application. Fig. 1 is a diagram of the apparatus first used in making these experiments. As the first runs were purely voltage determina-

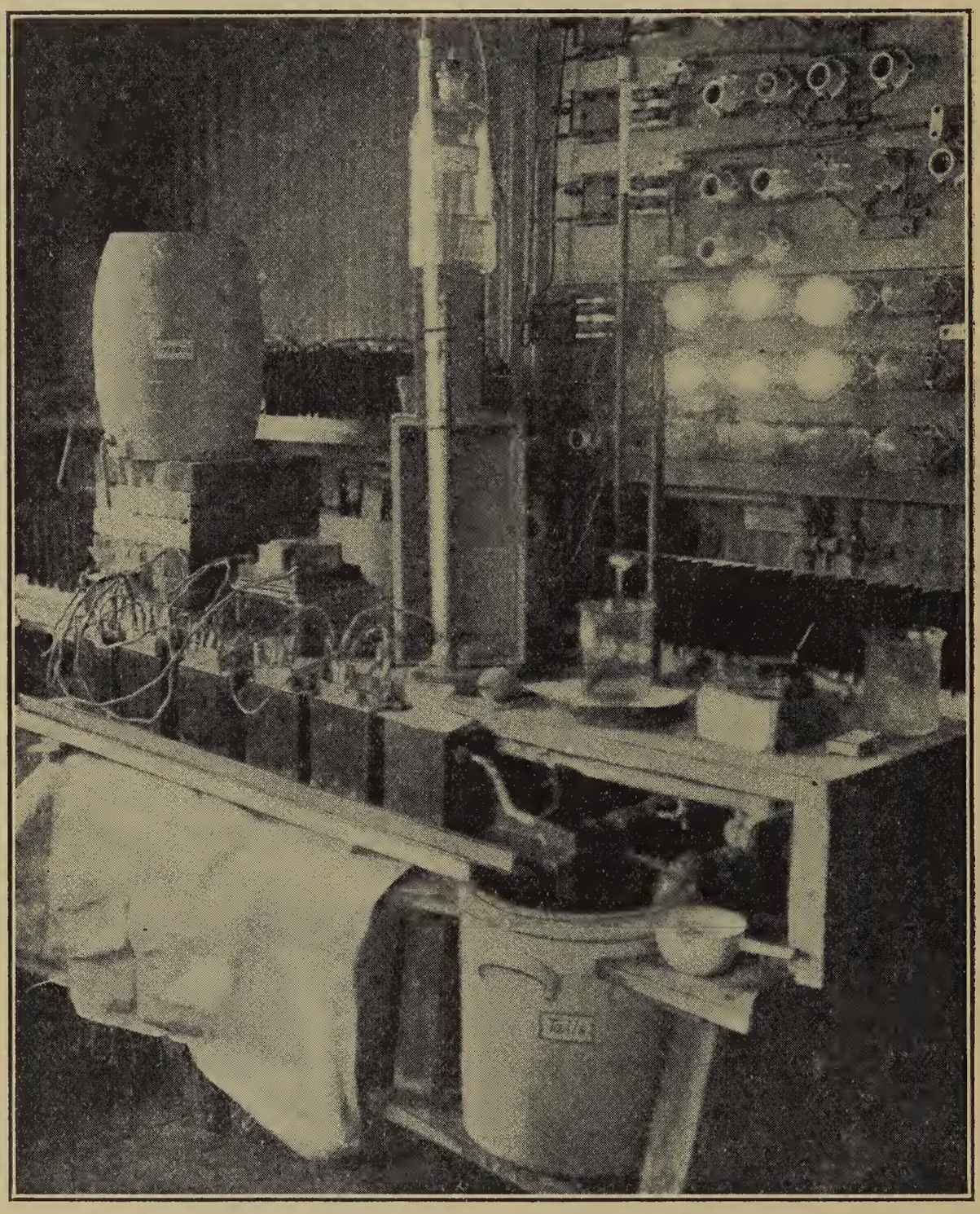


Fig. 2. Cell Arrangement for Efficiency Tests.

tions, agitation was dispensed with, a stirring rod being vigorously used at the time a reading was taken. Compressed roaster gas was at first used in the Pohlé lifts, but later air was sub-

stituted. After complete voltage records had been obtained for varying current density, composition of electrolyte, temperature, etc., the question of current efficiency was studied, several cells being connected in series and compressed air being introduced through a perforated false bottom in each cell. This general arrangement is shown in Fig. 2. Finally large cells were operated, using 600 amperes, as shown in Fig. 3, and compressed air was introduced at the bottom of each cell, through a 1½-inch (3.8 cm.) lead pipe, coiled in a spiral and perforated at regular intervals with eighty 3/64-inch. (1.2 mm.) holes. Measurements showed that the pressure necessary started barely above

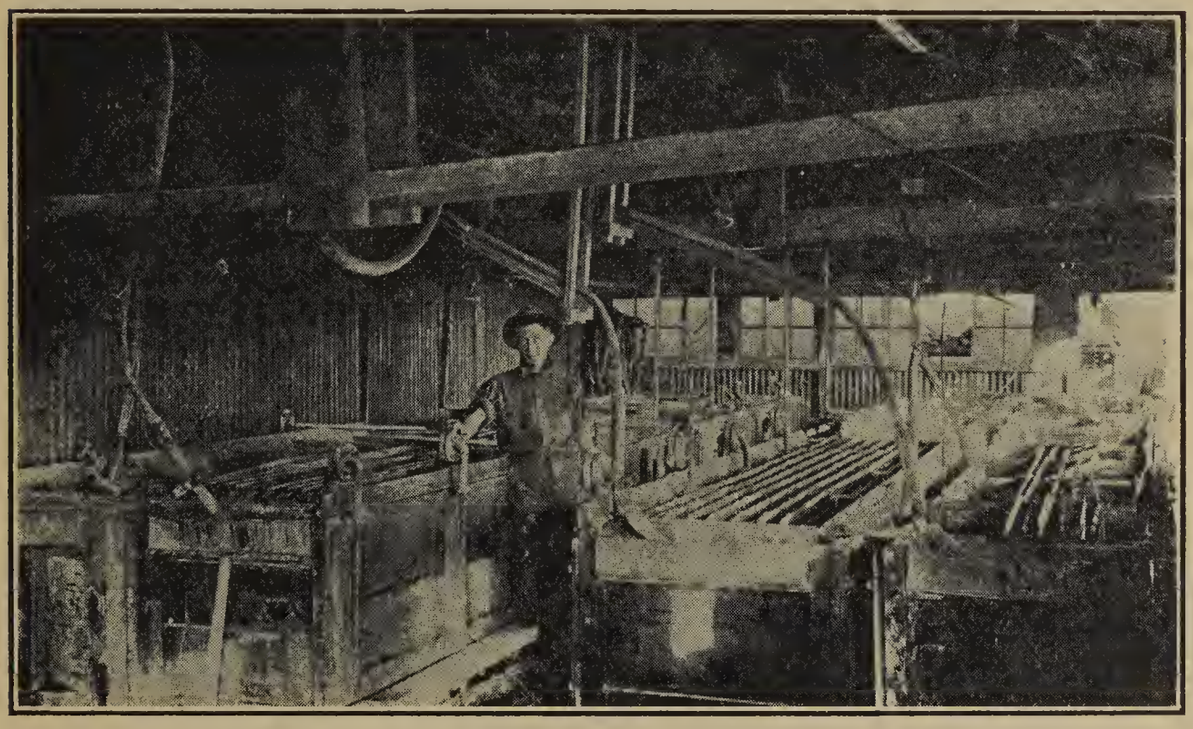
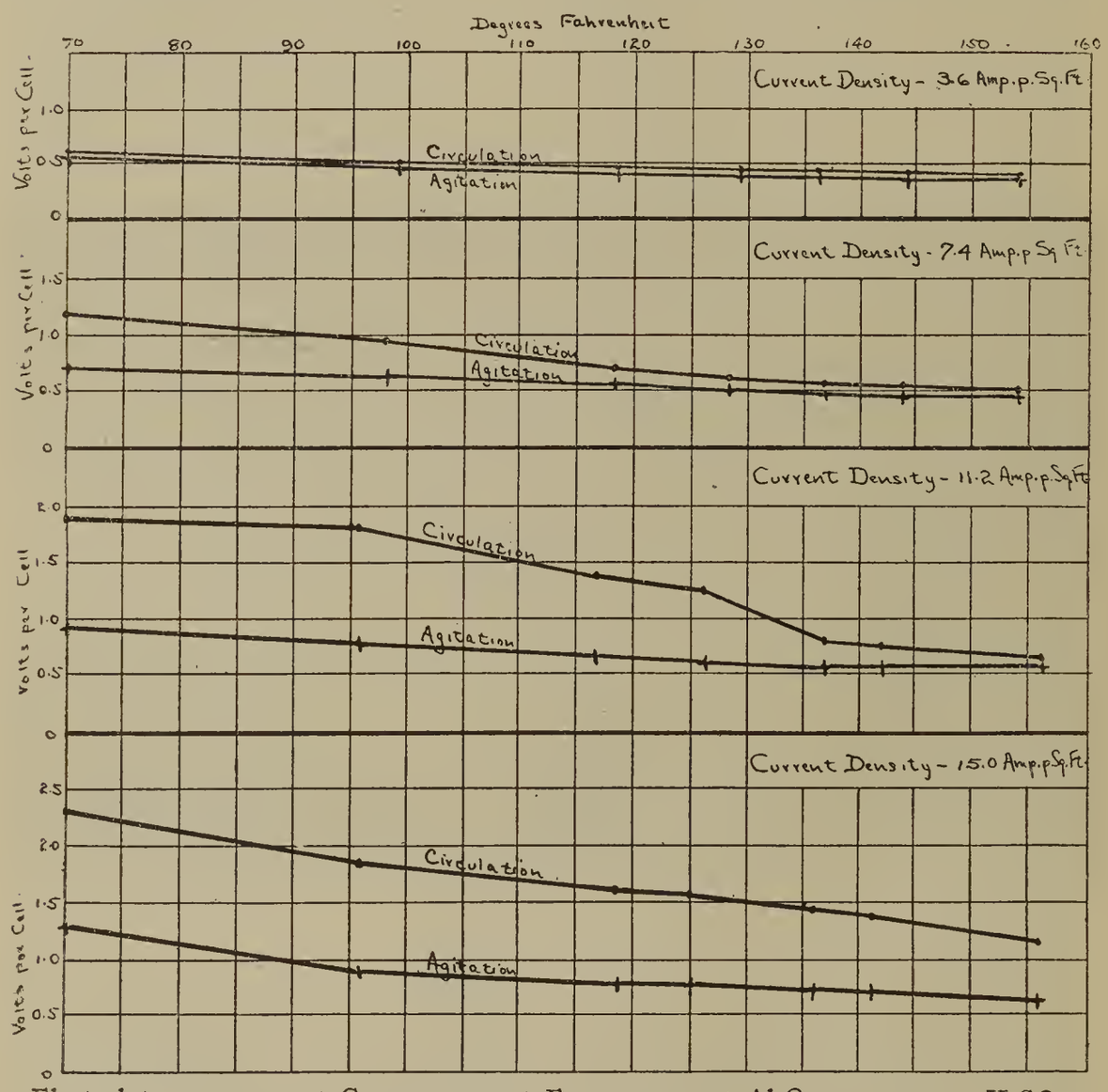


Fig. 3. Full Size Cells.

that of submergence or about 1½ inches (3.8 cm.) of mercury. Then as these holes gradually became choked by crystals or sediment, the pressure rose to about 3 inches (7.6 cm.) of mercury. This would take several hours. Then steam was introduced into the air system for several minutes, which fully cleared it. The quantity of air used was about 500 cubic feet (14 cub. m.) an hour, and as each cell deposited over a pound (453 gr.) of copper an hour, it will be seen that the power for compressing this air was very small.

The general plan of operation adopted was, therefore, a cir-

culation sufficient to replenish the liquor at a rate which would hold the anode oxidation product—ferric sulphate—at a concentration which would not seriously corrode the cathode, and compressed air agitation sufficient to obtain a minimum voltage by depolarization. An idea of these effects may be obtained from Fig. 4, which shows the voltages in one of the small cells with and without agitation for different current densities and tem-



Electrolyte—3.7 percent Cu, 2.0 percent Fe, 4.3 percent Al_2O_3, 4.2 percent H_2SO_4.

FIG. 4. Effect of Agitation upon Cell Voltage.

peratures. It will be noted that rising temperature assists the depolarization while rising current density impedes it.

ANODES AND DEPOLARIZATION.

Three commercially possible materials are today available for use as insoluble anodes in sulphate liquors: lead, magnetite and

carbon. There are two objections to lead, viz., it does not work at low cell voltages even in the presence of depolarizers, and its life is more or less limited, due to the flaking off of the sulphate and peroxide formed on its surface.

Magnetite is fragile and expensive and it remains to be seen whether it will hold its own in large scale work. The showing made at Chuquicamata will settle this point.

Carbon has been used for many years as an anode in chloride electrolytes and has given satisfactory service. In many of these cases free chlorine gas has been evolved at the anode, so that the disintegration of the carbon conglomerate in sulphate solu-

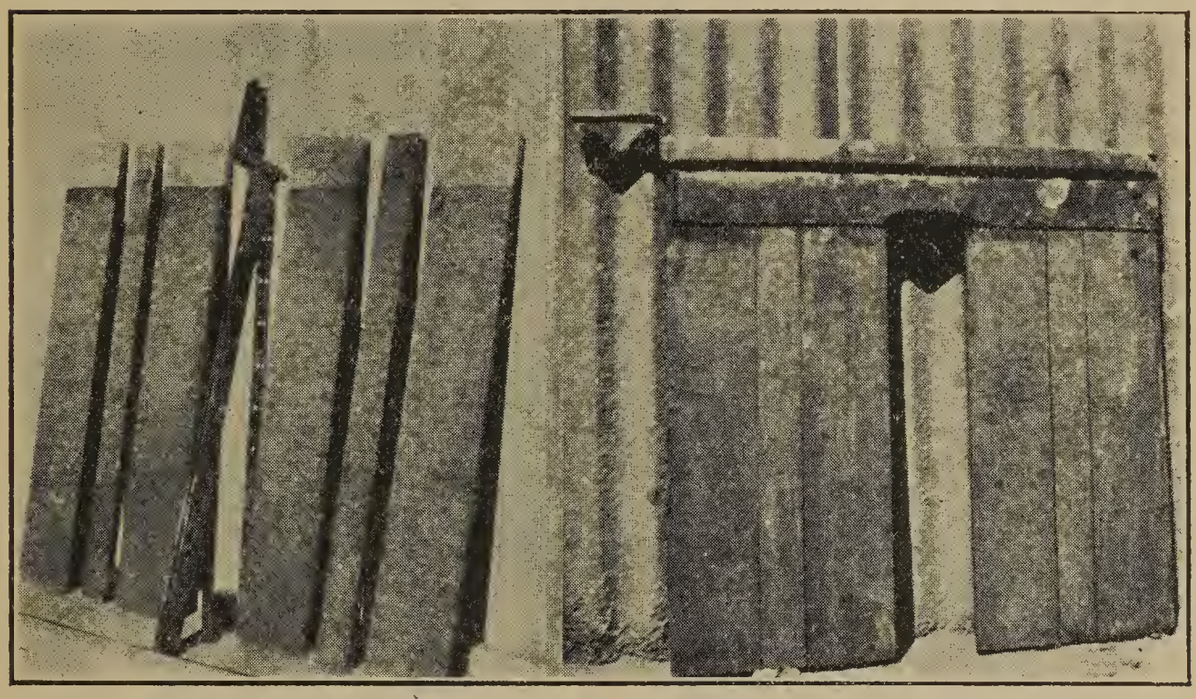


FIG. 5. Anode Parts. FIG. 6. Completed Anode.

tions must be due to the chemical properties of the oxygen formed, rather than to any physical attack. We know that charcoal, for example, has the property of absorbing large volumes of gases and we find that oxygen evolved at a carbon anode will react markedly with depolarizing agents, while oxygen liberated in the same way at a lead anode gives but partial response. It seems likely, therefore, that something akin to ozone is formed at the surface of the carbon anode, and that in the absence of substances susceptible of more ready oxidation, the carbon itself or its more or less carbonized binding material is oxidized and the anode breaks down.

The early work done with electrolytes weak in either sulphur dioxide or ferrous sulphate, showed a very decided softening of the surface of the anode. The later work, after ferrous sulphate was definitely adopted as the depolarizing agent, and a minimum of 1½ percent ferrous iron kept in contact with the anode by agitation, showed no sign of any deterioration of the anode after several months use. Nearly all of the work was done with Acheson graphite slabs, but some tests were made with baked carbon slabs and as far as these tests went, no difference was found in the behavior of the two.

The construction of a practical anode out of the ½ x 4 inch

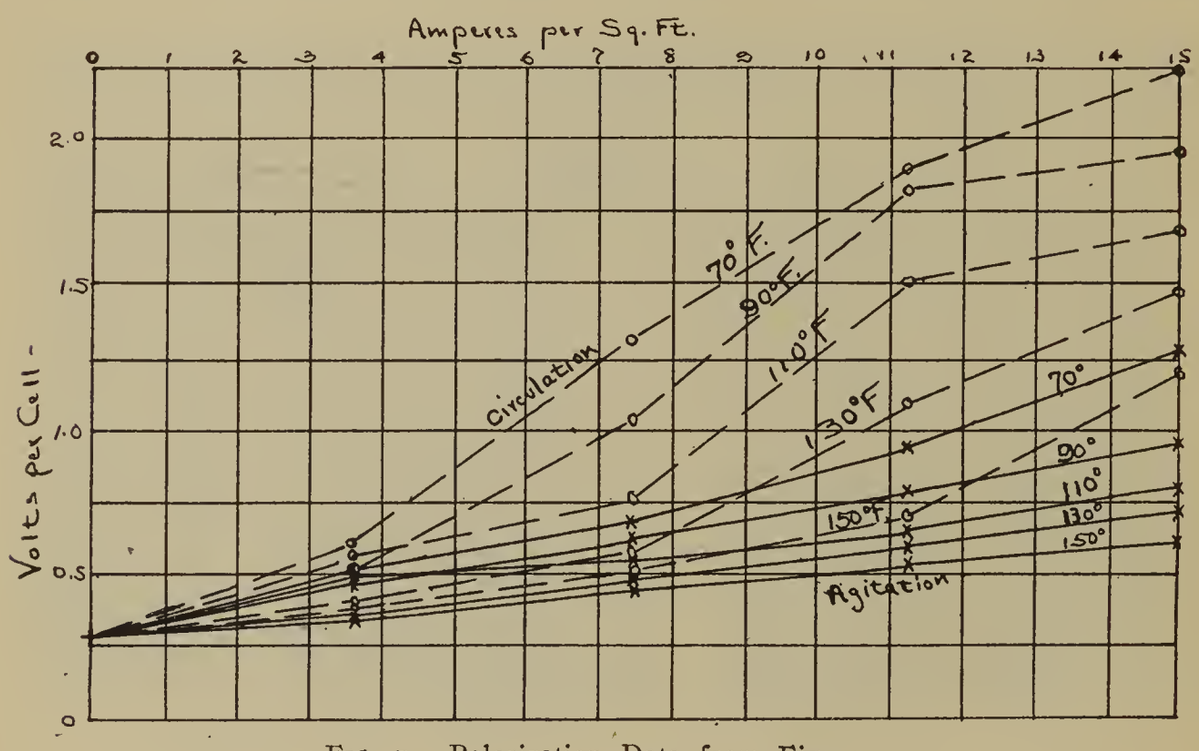


Fig. 7. Polarization Data from Fig. 4.

(1.25 x 10 cm.) slabs used gave some trouble. After several trials the design shown in Figs. 5 and 6 was developed and gave satisfactory service. The carbon strips were first trued up and the necessary holes drilled. Then they were electroplated with a thin film of copper at the upper end and the copper contact strips attached with copper bolts and nuts. The exposed copper parts were then given a coat of asphaltum paint and a lead apron burned around the entire upper end. This construction prevented the electrolyte from reaching the copper parts and dissolving them either chemically or electrolytically and the voltage drop between bus bar and active anode surface was negligible.

When a piece of carbon and a strip of copper are immersed in an acidulated copper sulphate solution, a voltmeter indicates an open circuit voltage of 0.29 volt, the carbon being, of course, electro-negative to the copper. This counter e.m.f. has, therefore, to be overcome when using carbon as an anode. The data given in Fig. 4 can be rearranged to show this; this is done in Fig. 7, and brings out clearly the effect of agitation, temperature and current density. No attempt has been made to measure actual polarization voltages or figure the theoretical voltages

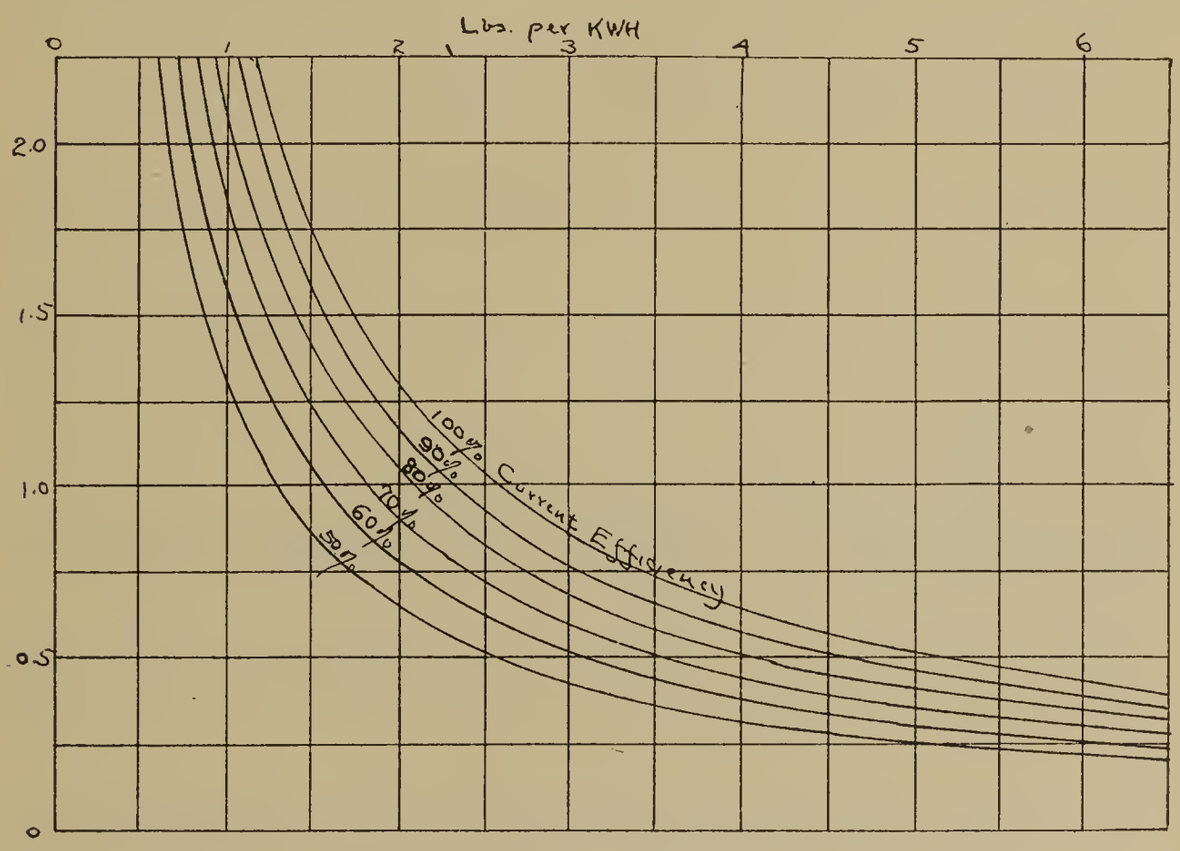


FIG. 8. Pounds Copper per K. W. H. for Various Voltages.

possible, but the solid lines in this diagram represent the actual voltages obtainable under corresponding working conditions. The liquors used in many of these measurements contained a few hundredths of a percent of free sulphur dioxide, but it is not believed that this has any bearing on the voltages obtained. All percentages by analysis given in this paper represent grams per 100 c. c., except when measuring the percentage of sulphur dioxide in roaster gas, which is stated by volume.

Next a series of investigations was undertaken on the effect of varying quantities of free acid, iron and alumina in the elec-

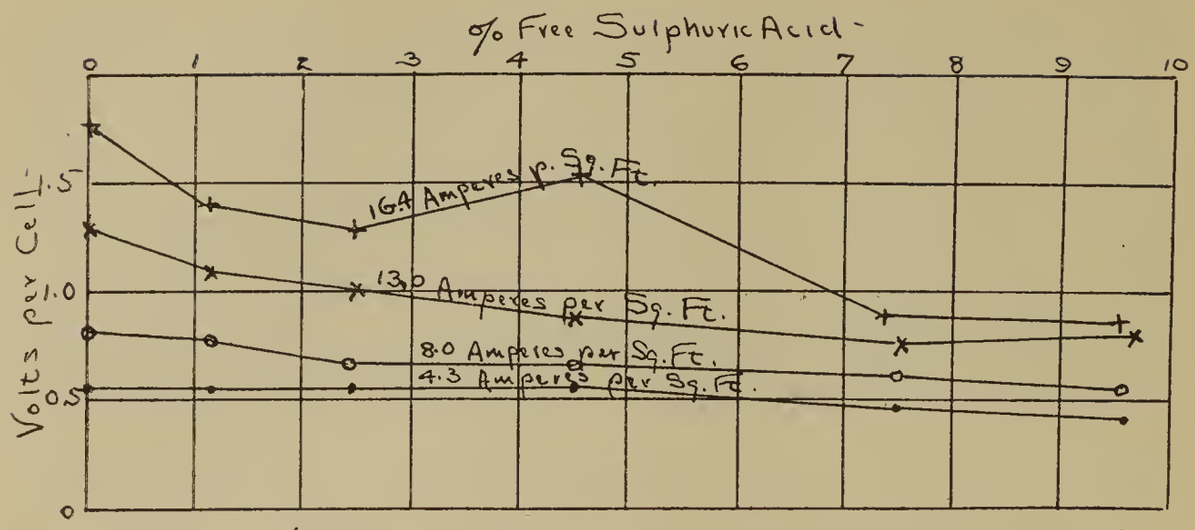


FIG. 9. VOLTAGE VS. FREE ACID - NO AGITATION - 120°F.

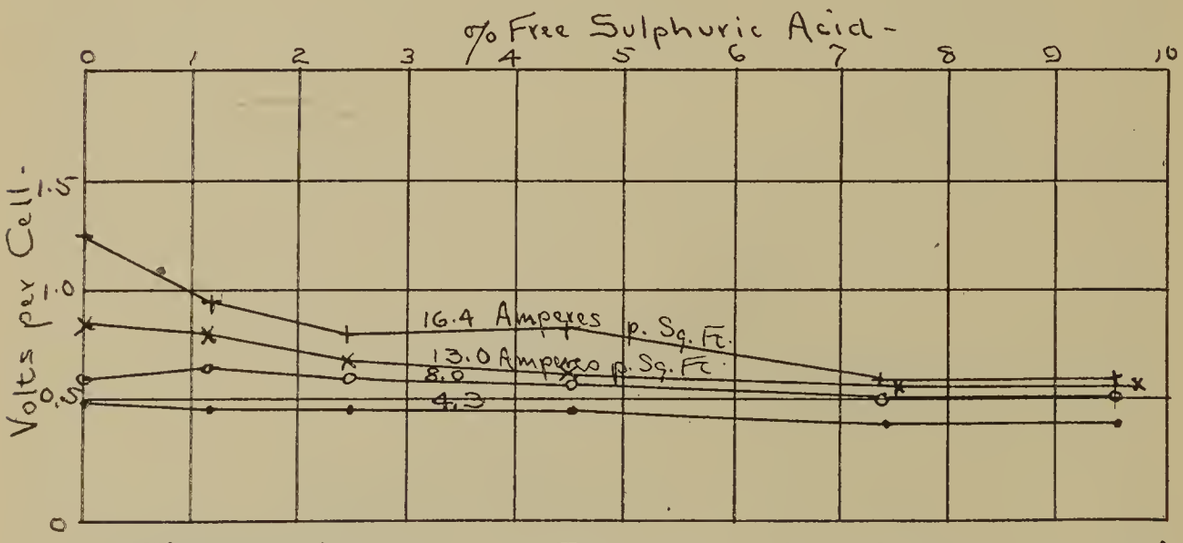


FIG. 10 - VOLTAGE VS. FREE ACID - WITH AGITATION - 120°F.

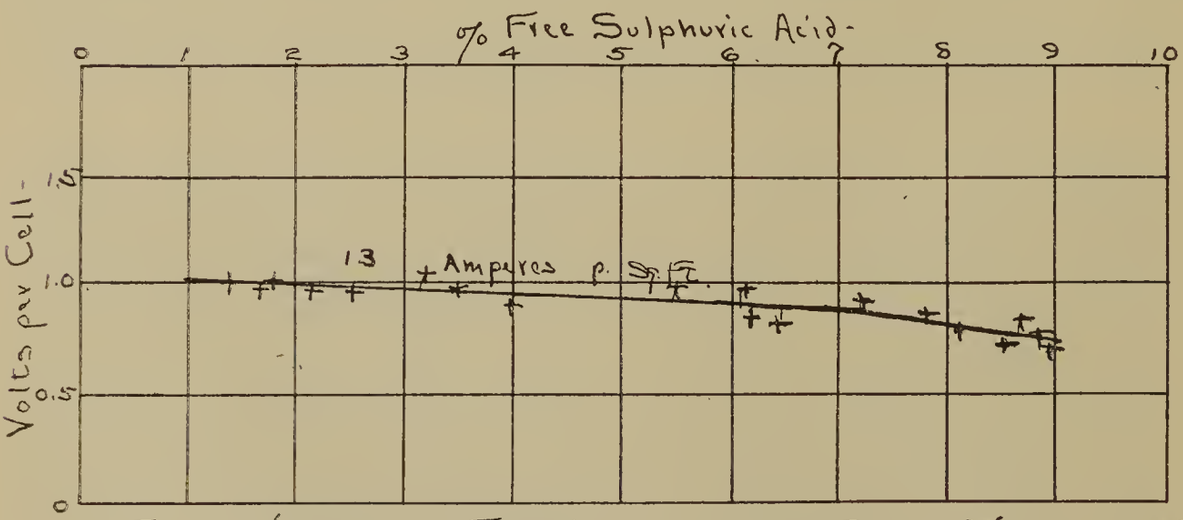
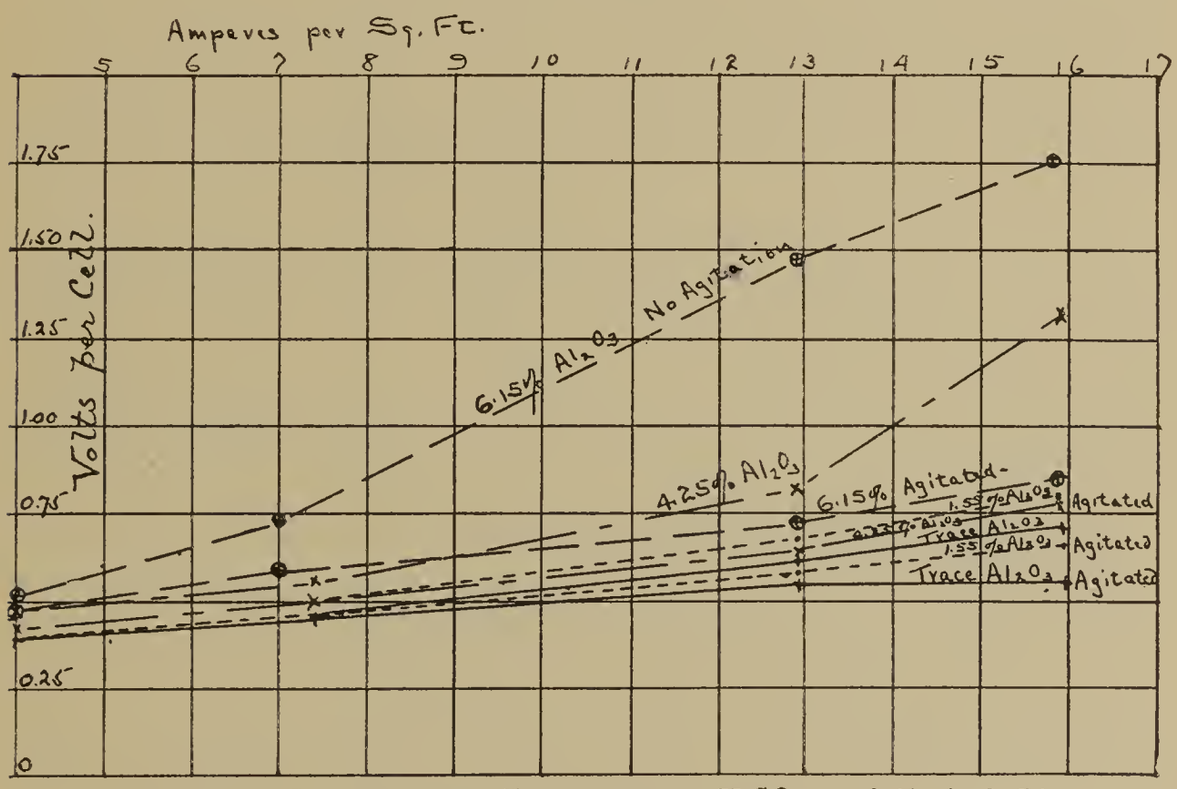


FIG. 11 - VOLTAGE VS FREE ACID - LARGE SCALE WORK - 119°F.

Electrolyte - 4.3 % Cu, 3.5 % Al_2O_3, 2.4 % Fe

trolyte upon the voltage obtainable. In order to keep this paper within reasonable length, but a few representative diagrams will be given from the great number of measurements made and tabulated. Fig. 8 shows the general relation between power and voltage and current efficiency in the electrolysis of cupric sulphate, for convenience in considering the possible recovery per K.W.H. under these various conditions.

Figs. 9 and 10 show the effect of varying the quantity of free sulphuric acid in the electrolyte at a constant temperature of 120° F. (49° C.). As increasing temperature was found of ma-



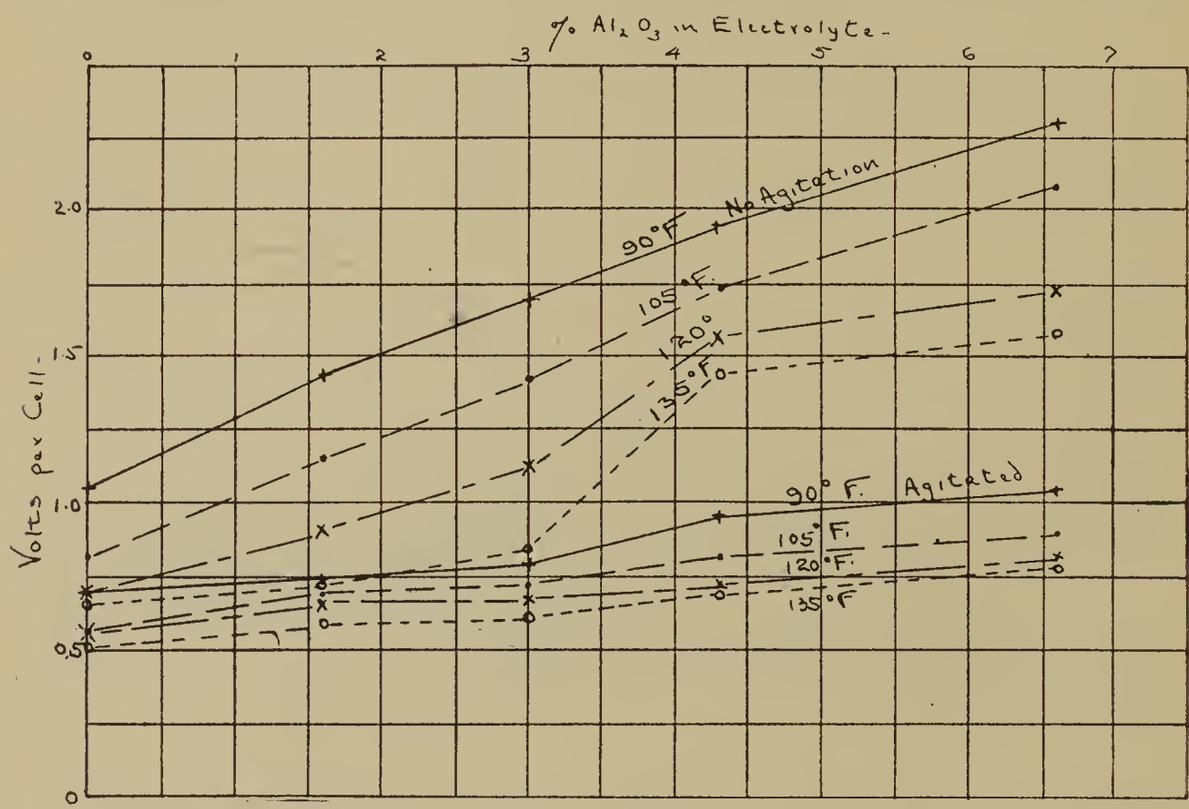
2.5 percent Cu, 3.3 percent Fe, 4.3 percent H_2SO_4, 120° F. (49° C.)

FIG. 12. Voltage *vs.* Alumina.

terial assistance both in reducing the ohmic resistance of the cell and in rendering efficient depolarization more easily obtainable, a cell temperature of about 115° F. (46° C.) was determined upon when large scale work was taken up. Too high a temperature, on the other hand, increased cathode corrosion, a matter which will be discussed later on. Fig. 11 shows the working voltages obtained with varying acidity in large scale work. It is evident that the acid assists somewhat in the mechanism of depolarization and lowers the resistance of the electrolyte, but that there is no warrant for carrying the high percentage

of acid used in regular refining work. The enormous quantity of salts present in the electrolytes used is doubtless the cause of this difference. Most of the work was, therefore, done at an acidity of not less than 4 percent. Too high an acid content impeded the solution of sulphur dioxide, as will be shown later.

Next the effect of aluminum sulphate was taken up and the results obtained at a temperature of 120° F. (49° C.) with varying current densities are shown in Fig. 12, and similar data for a fixed current density with different temperatures in Fig. 13.



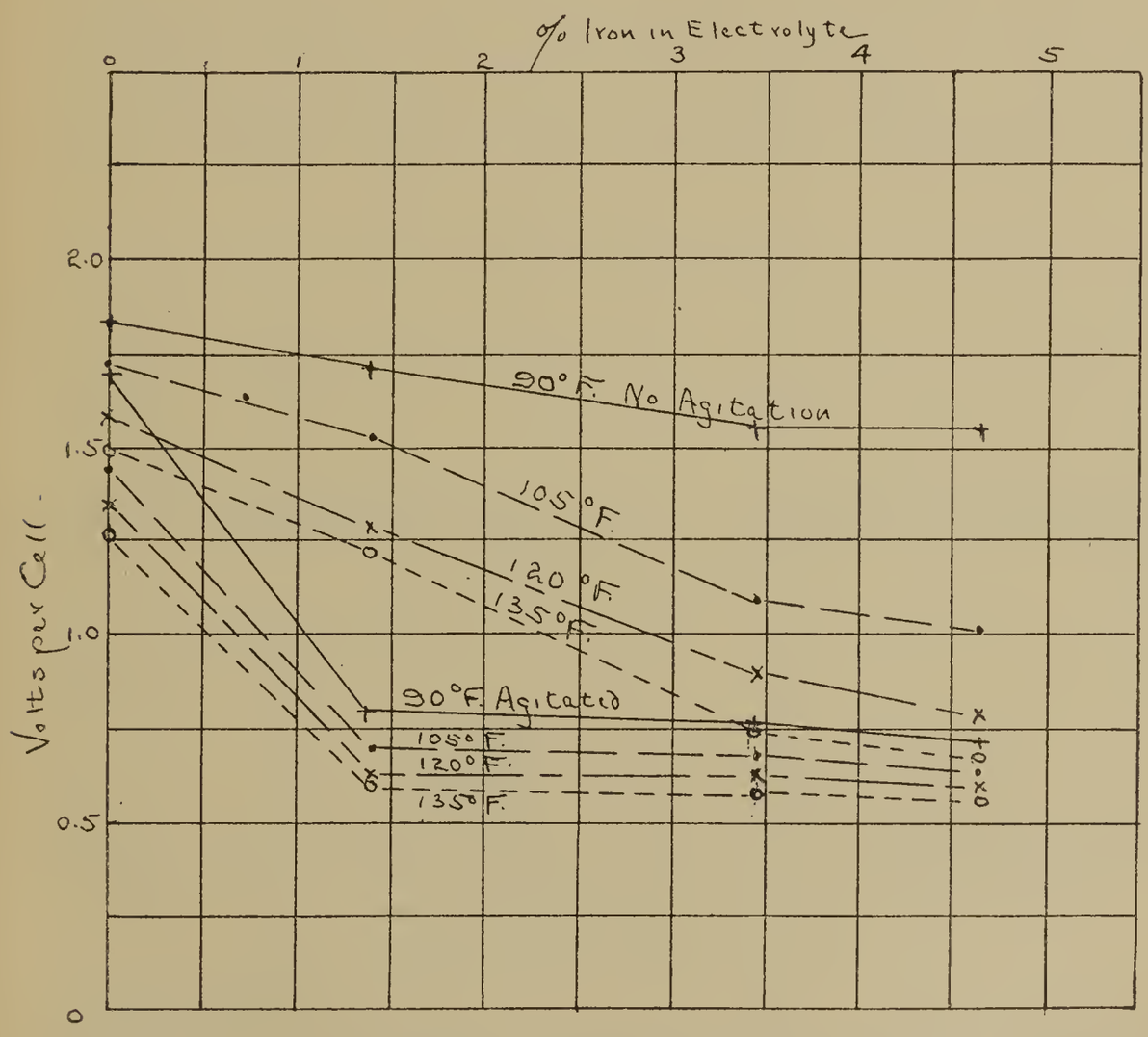
3.1 percent Cu, 2.4 percent Fe, 4.0 percent H_2SO_4, 15.7 Amp. p. Sq. Ft. (173 p. sq. m.)

FIG. 13. Voltage *vs.* Alumina.

These two sets of curves have been selected as representative of the general effect alumina has of interfering with depolarization. It was found in regular work that four percent was the maximum which could be carried in the electrolyte without excessive voltage, disportionate agitation or the production of soapy froth. On the other hand, it is desirable to carry as much as possible on account of its restraining effect upon cathode corrosion. It may be said here that a current density of 13 amperes per square foot (143 per sq. m.) was decided upon as causing about as rapid a production of oxygen at the anode as could be

properly handled by the depolarizing agent. Alumina also reduces the absorbing power of liquor for sulphur dioxide.

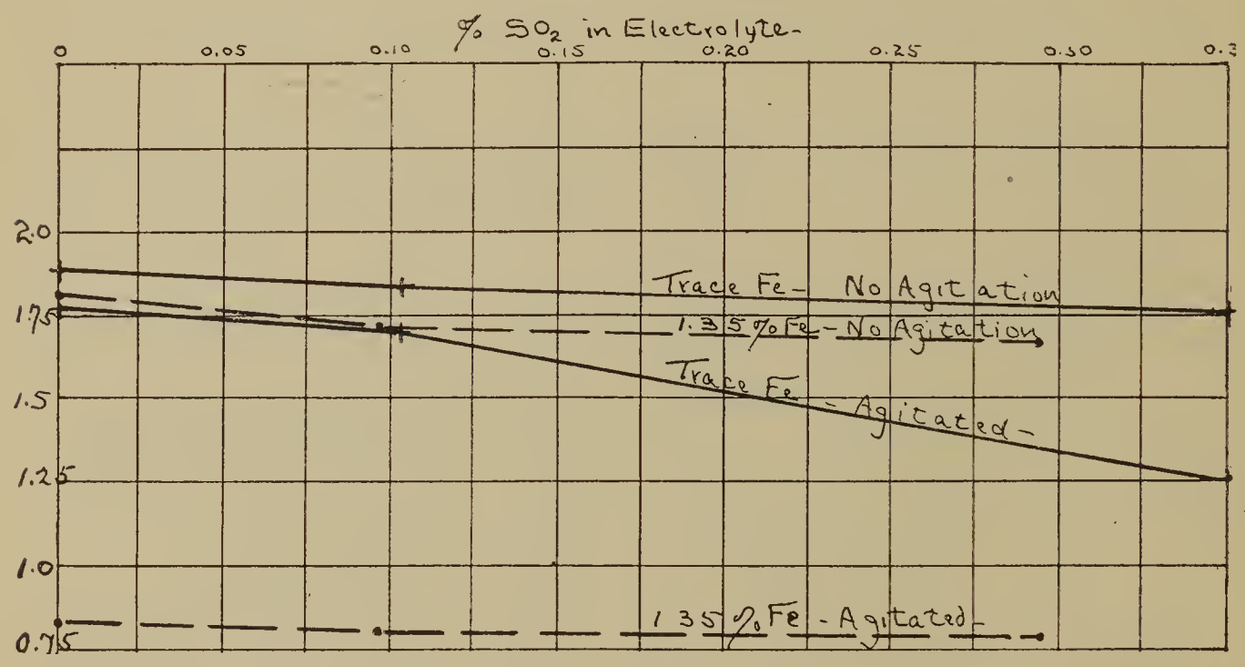
Next the effect of ferrous sulphate was studied. Fig. 14 shows that in the absence of agitation the voltage decreases in proportion to increasing concentration of ferrous iron but that except at high temperatures even very concentrated solutions give but partial depolarization. On the other hand, with agitation, the



2.6 percent Cu, 4.4 percent Al_2O_3, 4.2 percent H_2SO_4, 12.5 Amp. p. Sq. Ft. (137 p. sq. m.)
FIG. 14. Voltage *vs.* Iron.

voltage drops immediately as iron is introduced, to a minimum which is practically unaffected by further additions. No ill effect is produced by very high iron. The reason that agitation slightly lowers the voltage on the zero iron line is probably that the small quantities of sulphur dioxide present in the solutions have a slight depolarizing effect.

The relative values of sulphur dioxide and ferrous sulphate as depolarizing agents is taken up in Fig. 15. A solution showing but the merest trace of iron present by analysis was examined with varying proportions of sulphur dioxide added. Then sufficient ferrous sulphate was added to make the iron content 1.35 percent. At 90° F. (32° C.) and 13.2 amperes per square foot (145 per sq. m.), and in the absence of either ferrous iron or sulphur dioxide a voltage of nearly 1.9 is observed. Agitation drops this slightly, to about 1.8 volts. Adding SO_2 up to a content of 0.35 percent has but little effect in the absence of agitation, but when agitated the cell voltage drops steadily as the strength of SO_2 increases. 0.35 percent, however, brings



2.6 percent Cu, 4.3 percent Al_2O_3, 4.2 percent H_2SO_4, 90° F., 13.2 Amp p. Sq. Ft. (145 p. sq. m.)

FIG. 15. Voltage *vs.* Sulphur Dioxide.

the voltage down to but 1.25, and apparently a high content would be necessary to effect anything like the depolarization corresponding to the complete utilization of the anode oxygen. On the other hand, the moment any ferrous sulphate is added, the voltage drops to the value expected. It was, therefore, concluded that the presence in the liquor of the small quantities of sulphur dioxide which it is possible to absorb from relatively weak roaster gases, afforded no gain in depolarizing, while introducing various handicaps in other directions, so that ferrous

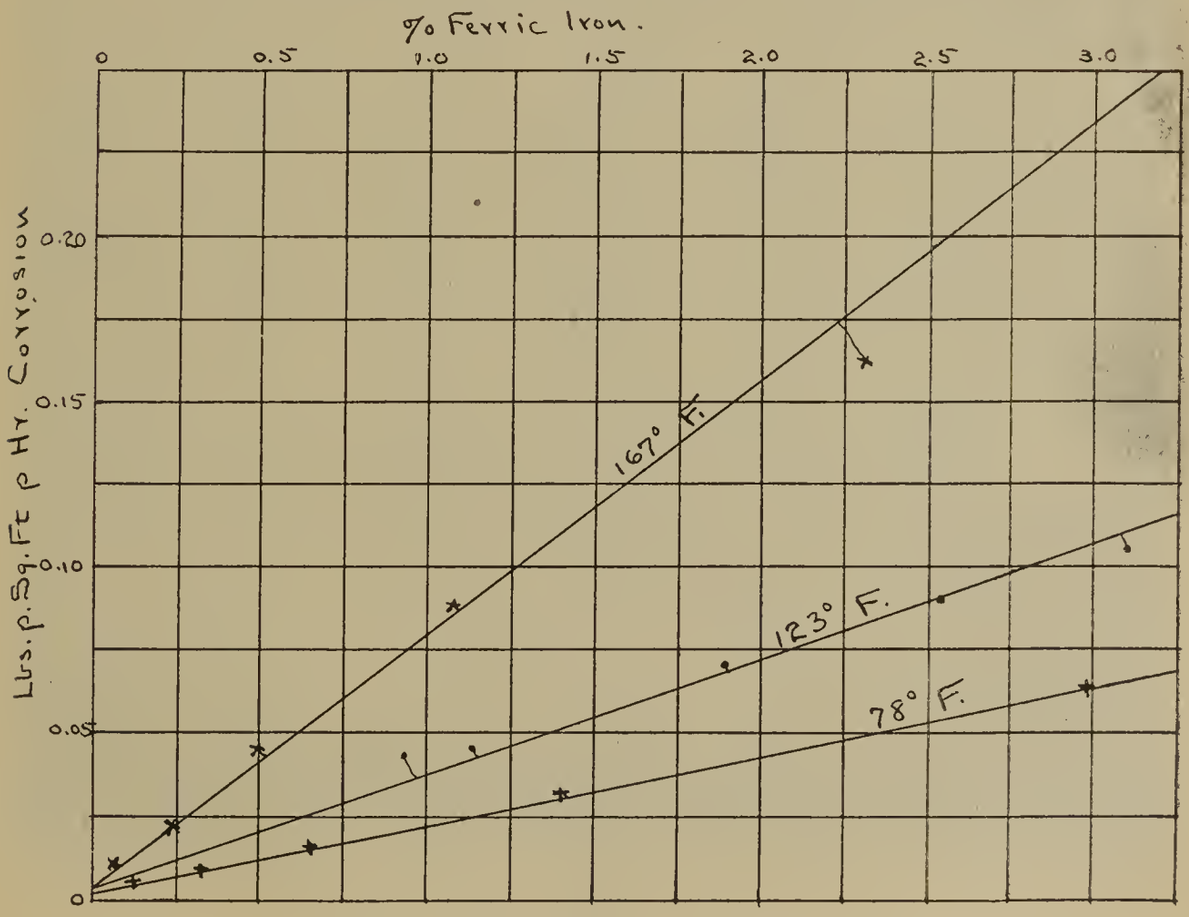
sulphate was settled upon as the depolarizing agent and a minimum of 1.5 percent ferrous iron determined upon.

CATHODES AND CORROSION.

Two problems were encountered at the cathode. The corrosive effect of the ferric sulphate produced at the anode made it difficult to obtain a high current efficiency, and under certain conditions the deposit would be tarnished by a film of copper sulphide.

The first difficulty is expressed by the reaction

$$Cu + Fe_2 (SO_4)_3 = CuSO_4 + 2\ FeSO_4.$$



Liquor: 4 percent H_2SO_4 + X $Fe_2 (SO_4)_3$
FIG. 16. Reduction of Ferric Sulphate by Copper.

Fig. 16 shows the corrosion rate to be expected in an acid solution of ferric sulphate. It is self-evident that the corrosion may be expressed in terms of weight lost per unit of superficial area of copper exposed to the wash of the liquor. It will be noted that the speed of the reaction is proportional to the concentration of ferric iron and is greatly accelerated by heat.

The rates of corrosion were measured in the motor-driven shaking machine shown in Fig. 17. This same apparatus was also used in the determination of the ferric iron in liquors. When simply a rate of corrosion was desired, the liquor was taken in such quantity that a measurable loss in the weight of the copper strip was obtainable without serious change to the strength of the liquor. When the ferric iron contents of the

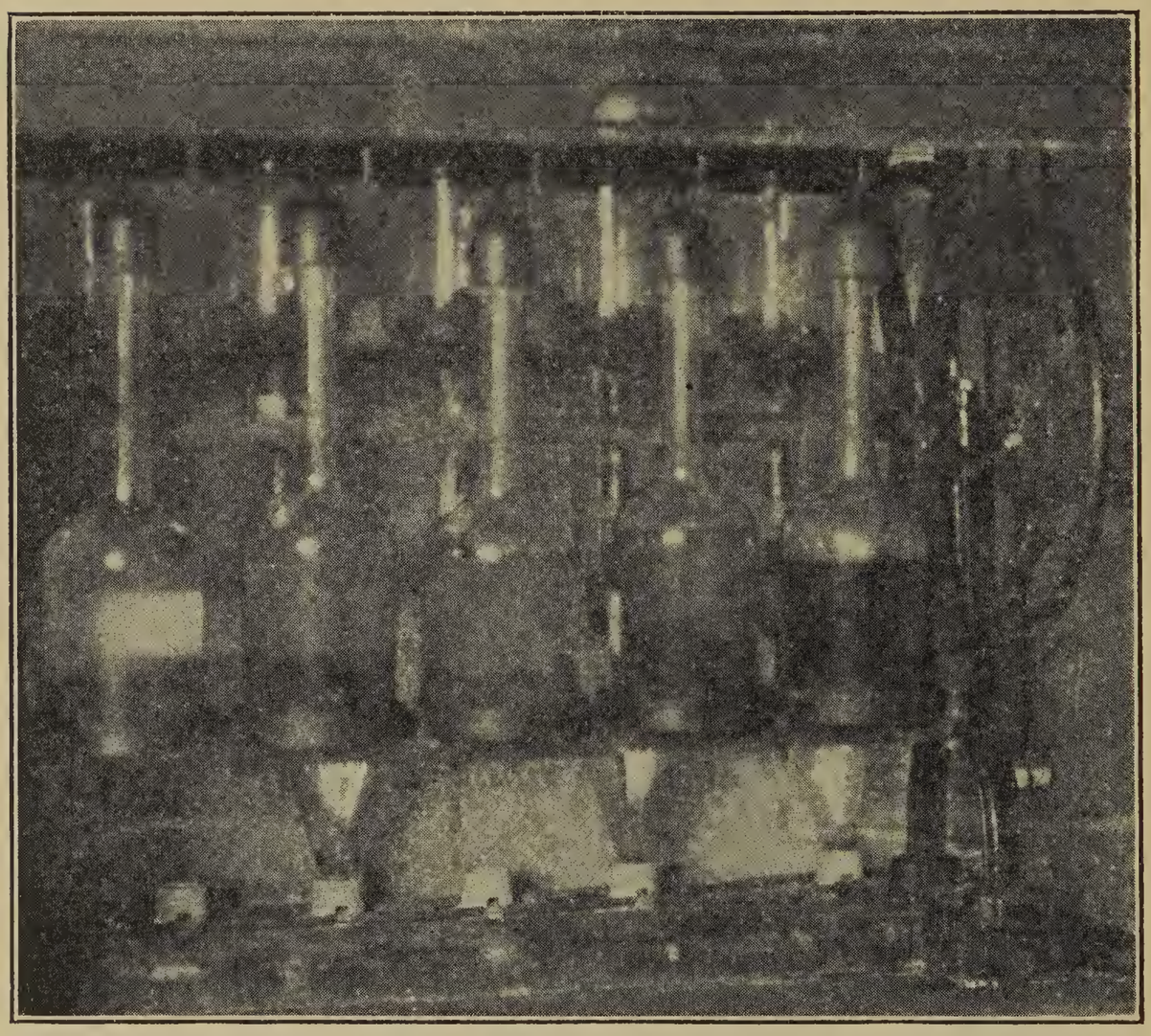
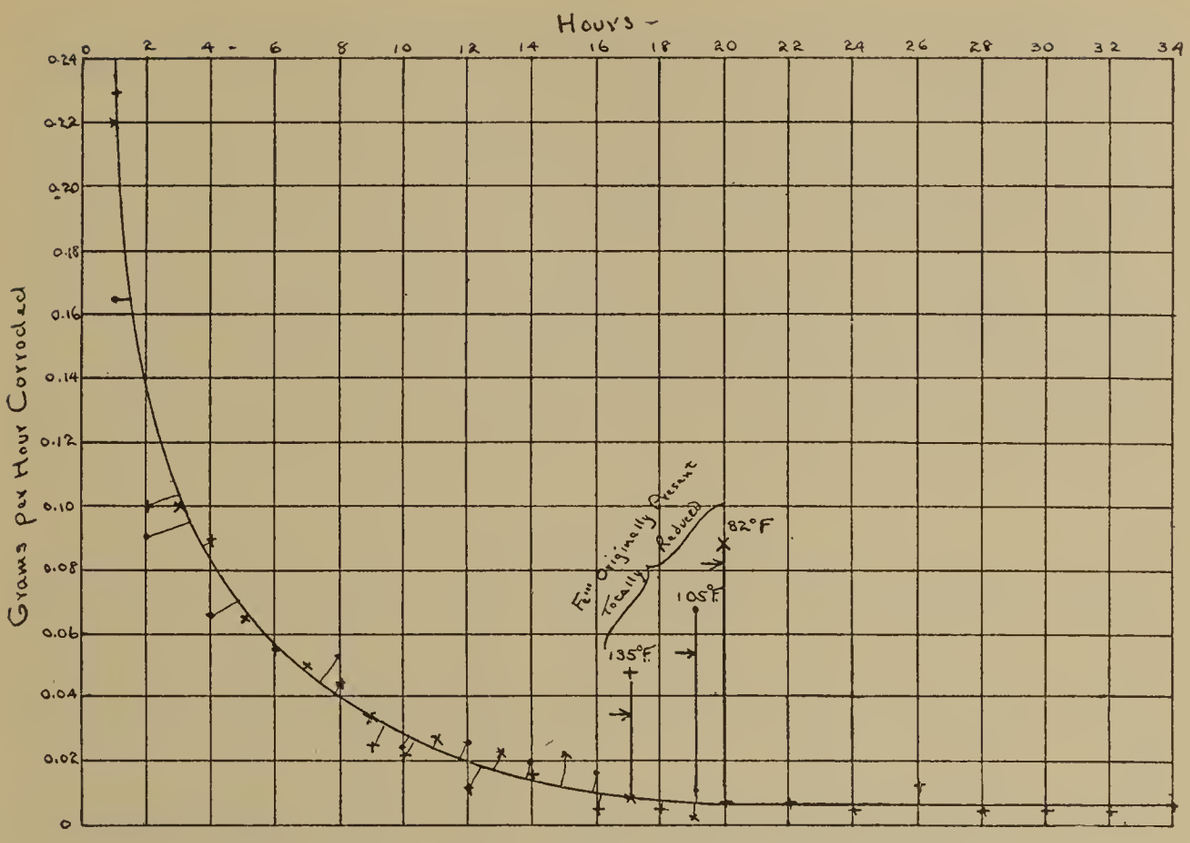


Fig. 17. Shaking Machine.

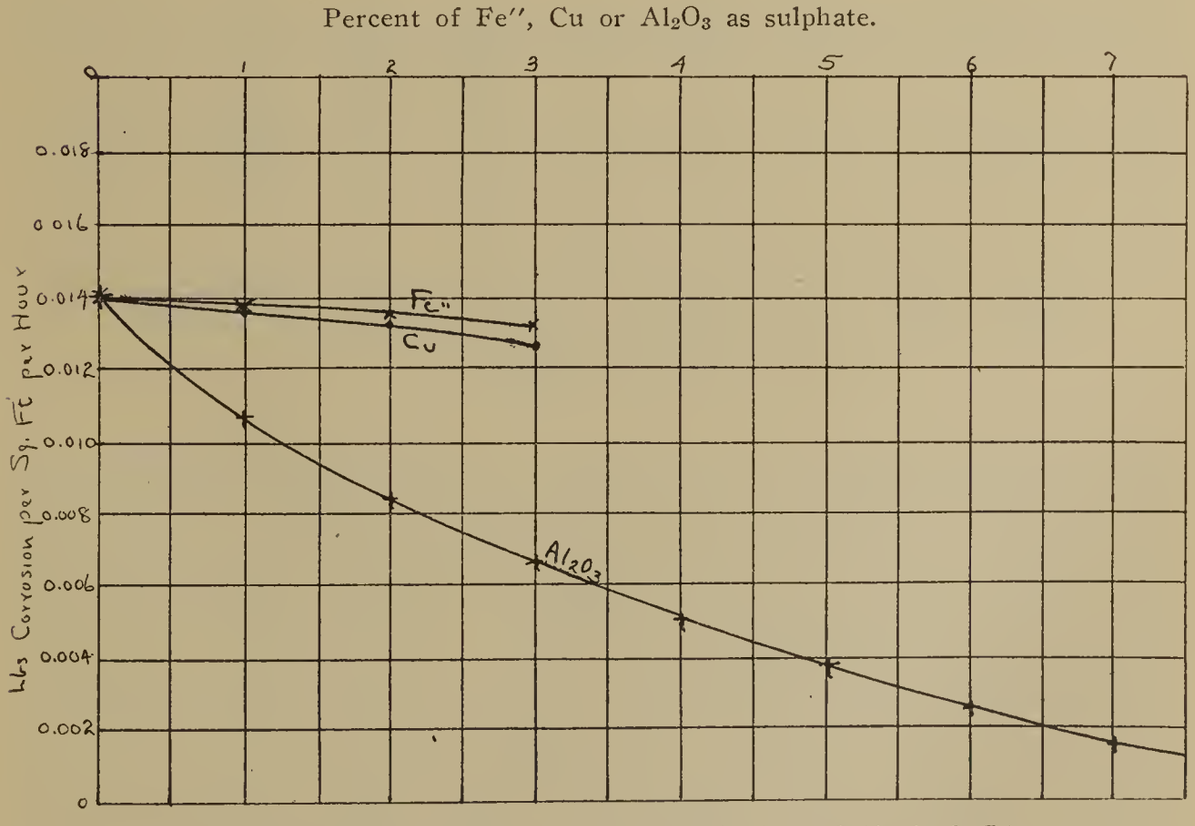
liquor was to be determined, on the other hand, the quantity of liquor was chosen so that complete exhaustion would not take an unreasonable time. Fig. 18 gives the characteristics of the machine. The oxidation error shown by constant loss in weight of the strip after 20 hours is very small.

The corrosion rates shown in Fig. 16 are very large. Thirteen amperes per square foot (143 per sq. m.) would deposit 0.034



Liquor: 3 percent Cu, 3 percent Al_2O_3, 4 percent H_2SO_4, 2 percent Fe'', 1.4 percent Fe'''. Copper Strip 2½ sq. inches surface.

FIG. 18. Oxidation Error of Shaking Machine.

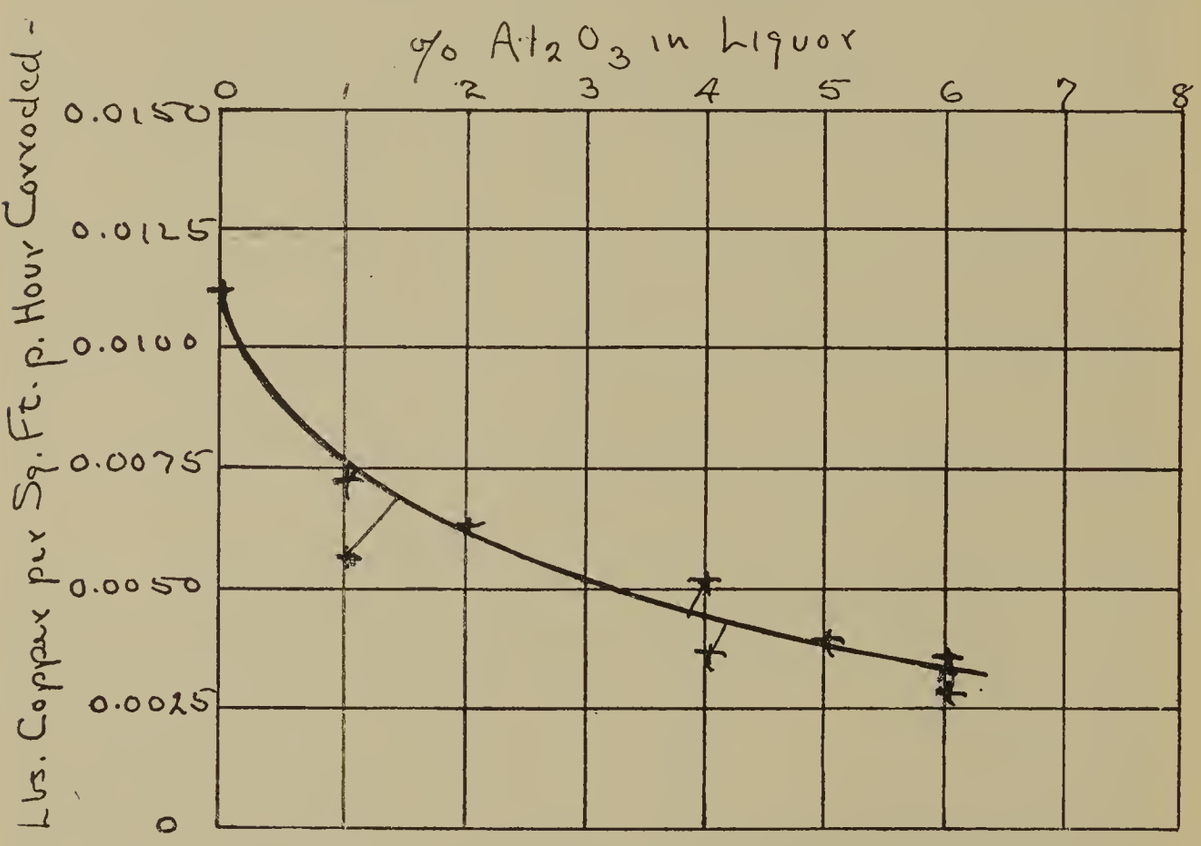


Liquor: 4 percent H_2SO_4, 0.2 percent Fe''', 105° F. (41° C.)

FIG. 19. Relative Effects of Copper, Iron and Alumina on Corrosion.

lb. on a square foot (169 gr. per sq. m.) in an hour. From the diagram it appears that about 0.75 percent ferric iron at 123° F. (51° C.) would corrode as fast as the current deposited. A study was, therefore, made of the possible effects of the other components in the solution with quite remarkable results.

Fig. 19 shows the effect upon corrosion by adding either cupric, ferrous or aluminum sulphate to a liquor carrying 0.2 percent iron as ferric sulphate and 4 percent sulphuric acid. The copper and iron have but a slightly depressant effect upon



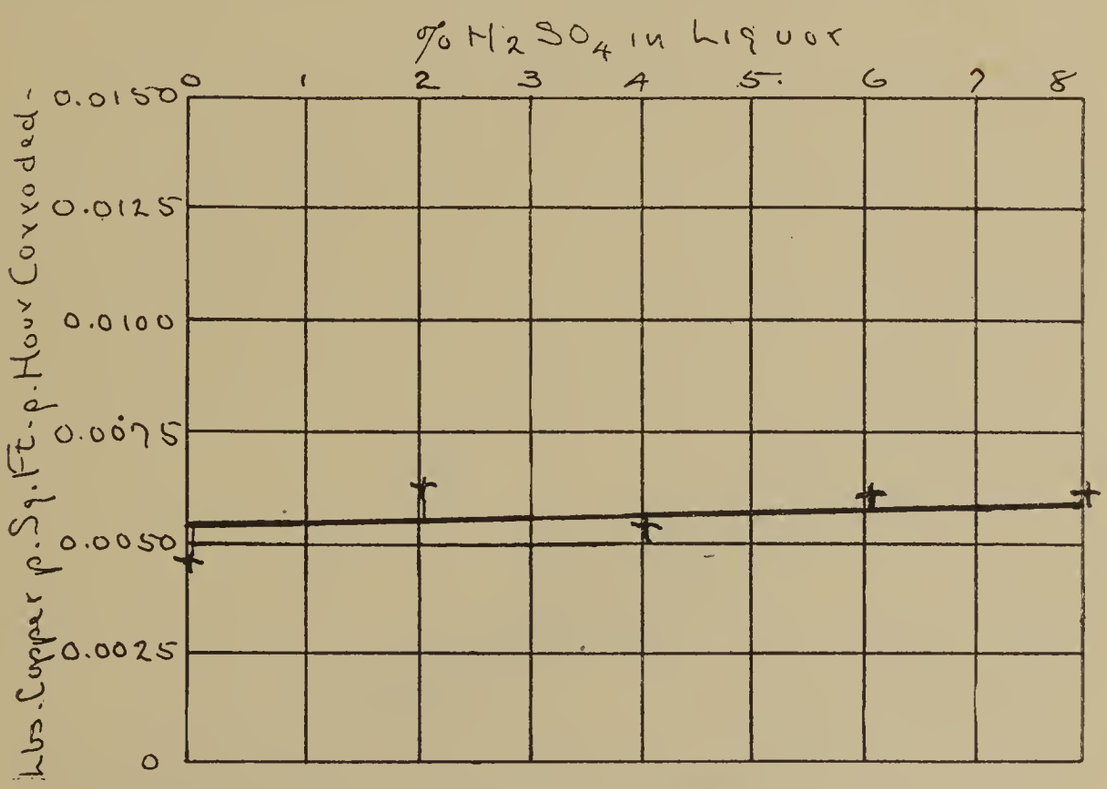
Liquor: 3 percent Cu, 3 percent Fe'', 0.2 percent Fe''', 4 percent H_2SO_4, 105° F. (41° C.)

FIG. 20. Effect of Aluminum Sulphate Upon Corrosion.

the speed of reaction of the ferric iron upon the copper strip; the alumina, however, has a most marked effect and when the solution is practically saturated with aluminum sulphate the corrosion is almost completely arrested. Fig. 20 shows this same relation for a liquor carrying 3 percent of both cupric and ferrous sulphates, being within the range of composition of a practical electrolyte. Fig. 21 shows that the amount of free acid present has but very slight effect. It, therefore, was determined to use aluminum sulphate as an antidote to ferric sul-

phate and it is believed this property of alumina may have wide application. No explanation is offered of the mechanism of this effect. It seems to slow down various reactions; for example, copper appears to cement upon iron with more difficulty. With alumina present, it is more difficult to depolarize, less sulphur dioxide can be absorbed, etc.

The second general difficulty, that of obtaining a bright deposit, was found to be due to the operation of several side reactions depositing either cupric sulphide or cuprous chloride upon the cathode. In the first place the work was done where the climatic



Liquor: 3 percent Cu, 3 percent Fe'', 0.2 percent Fe''', 3 percent Al_2O_3; 105° F. (41° C.)

FIG. 21. Effect of Free Acid Upon Corrosion.

conditions caused a tremendous amount of evaporation—some 200 units of water per unit of copper deposited had to be replaced—and the local water was full of salts, mainly chlorides. The electrolyte, therefore, rapidly built up in chlorides until about 0.1 percent Cl was found to be present by analysis. This resulted in a precipitation of cuprous chloride on the cathode which, owing to its actinic property, caused a tendency to blacken upon exposure to the light. Chlorine further reacted with the SO_2 when it was present in the liquors to form a cupric sulphide

film on copper. Finally unless the reduction of ferric sulphate by sulphur dioxide was carried out under proper conditions, some unknown practical products of reduction were formed which appeared to reduce to cupric sulphide at the cathode.

A brilliant deposit can easily be obtained where the liquor in the cells is free from chlorides or sulphur dioxide and any previous reduction of ferric sulphate has been properly carried out.

SULPHUR DIOXIDE AND REDUCTION OF FERRIC SULPHATE.

In Fig. 22 is given some data regarding the solubility of sulphur dioxide. In common with other gases its solubility varies

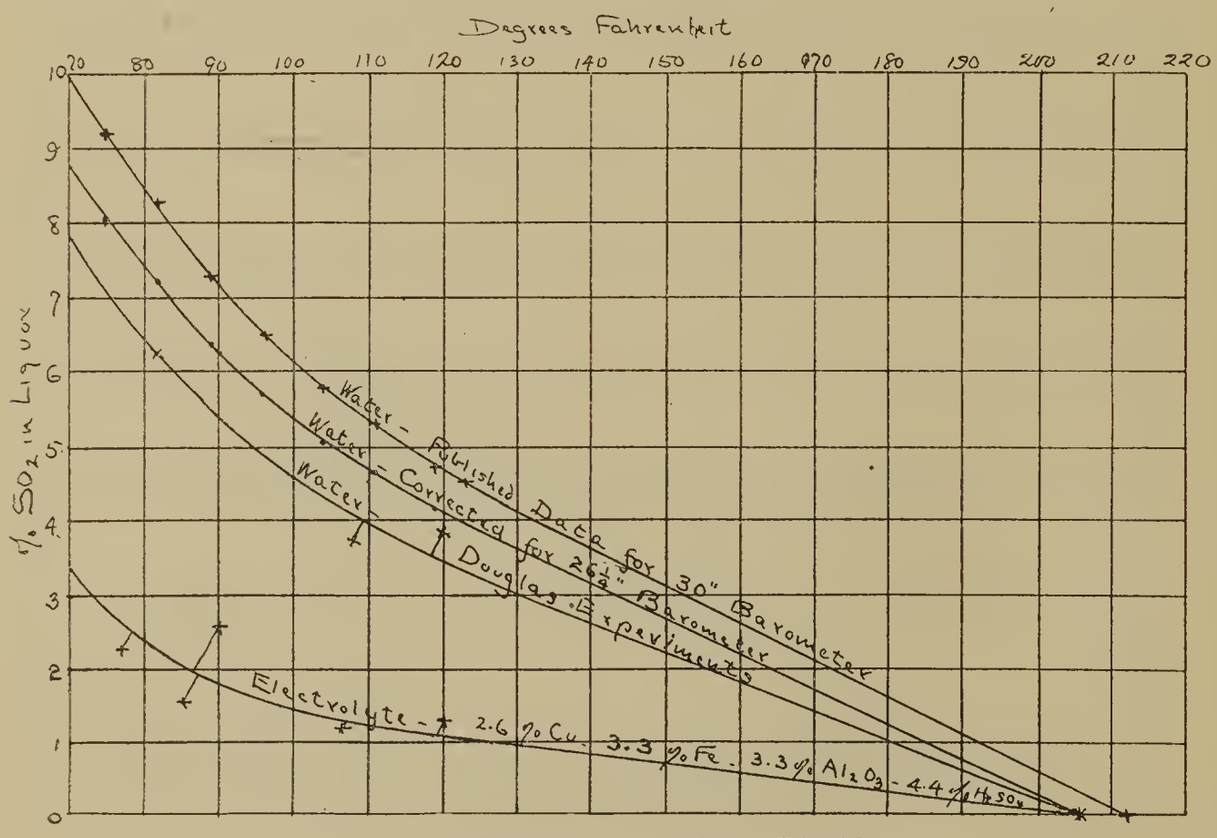


FIG. 22. Solubility of Sulphur Dioxide.

directly with the pressure and diminishes with increase of temperature until practically none remains in solution at the boiling point of the solvent. The curves in Fig. 22 are all for pure SO_2 gas at atmospheric pressure. The top curve is plotted from data in the published handbooks for the solubility of 100 percent SO_2 in water at various temperatures at sea level and the next one corrects these data to the 26.25 inch (668 mm.) barometer under which the local experiments were made. The next lower curve shows the results obtained by simply bubbling gas through

water until no further increase in dissolved SO_2 could be found by titration with iodine. The bottom curve gives the results of similar work using electrolyte as the solvent and a great decrease in the amount of SO_2 which can be absorbed will be noted. Of course, if the gas used runs less than 100 percent SO_2, a corresponding diminution of the absorption value will be noted and Fig. 23 is a rearrangement of some of the data in Fig. 22 which shows just what can be expected with various strengths of roaster gas.

Figs. 24 and 25 are examples from a complete set of tests

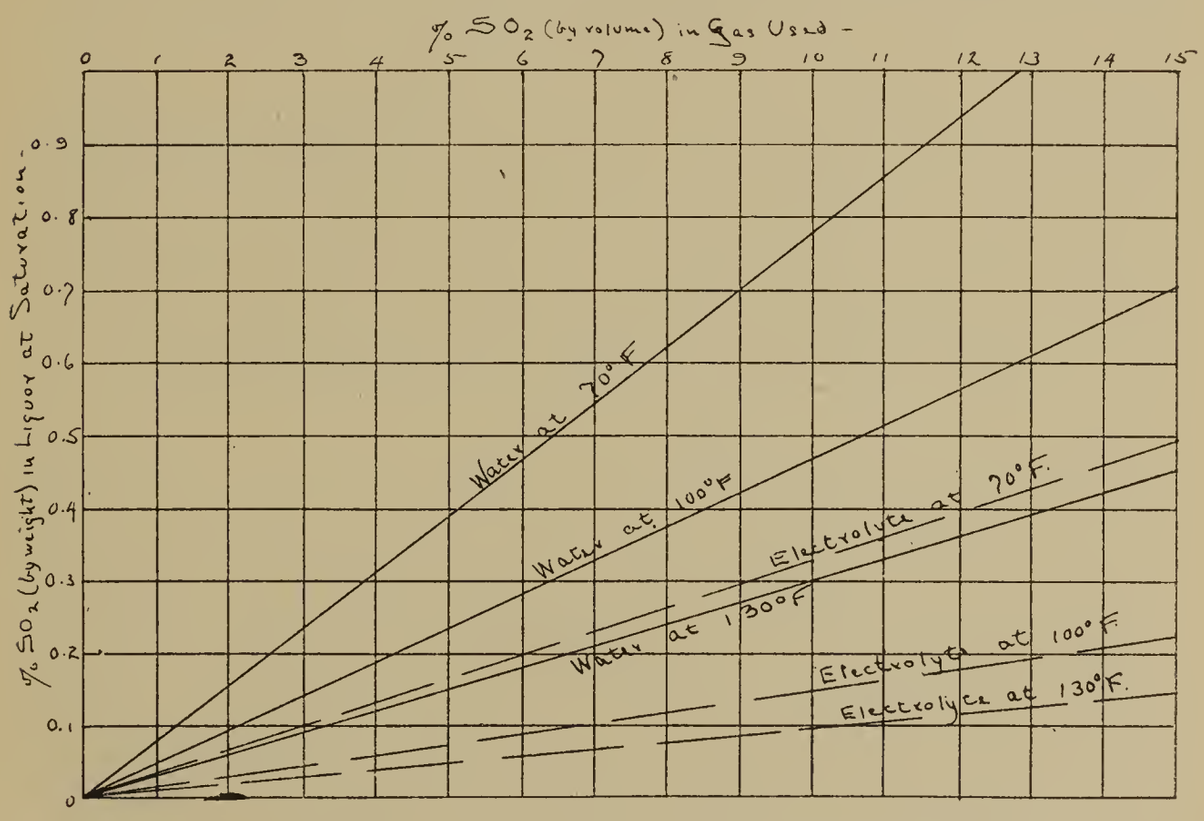
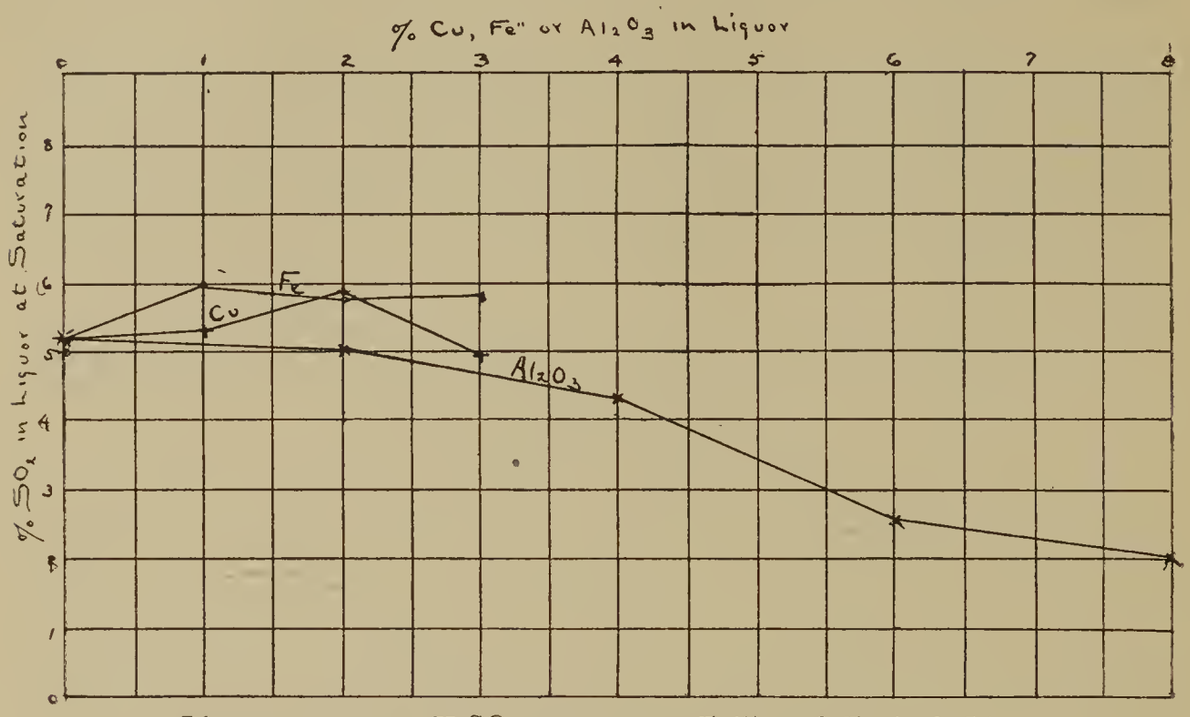


FIG. 23. Application of Henry's Law of Partial Pressures to Fig. 22.

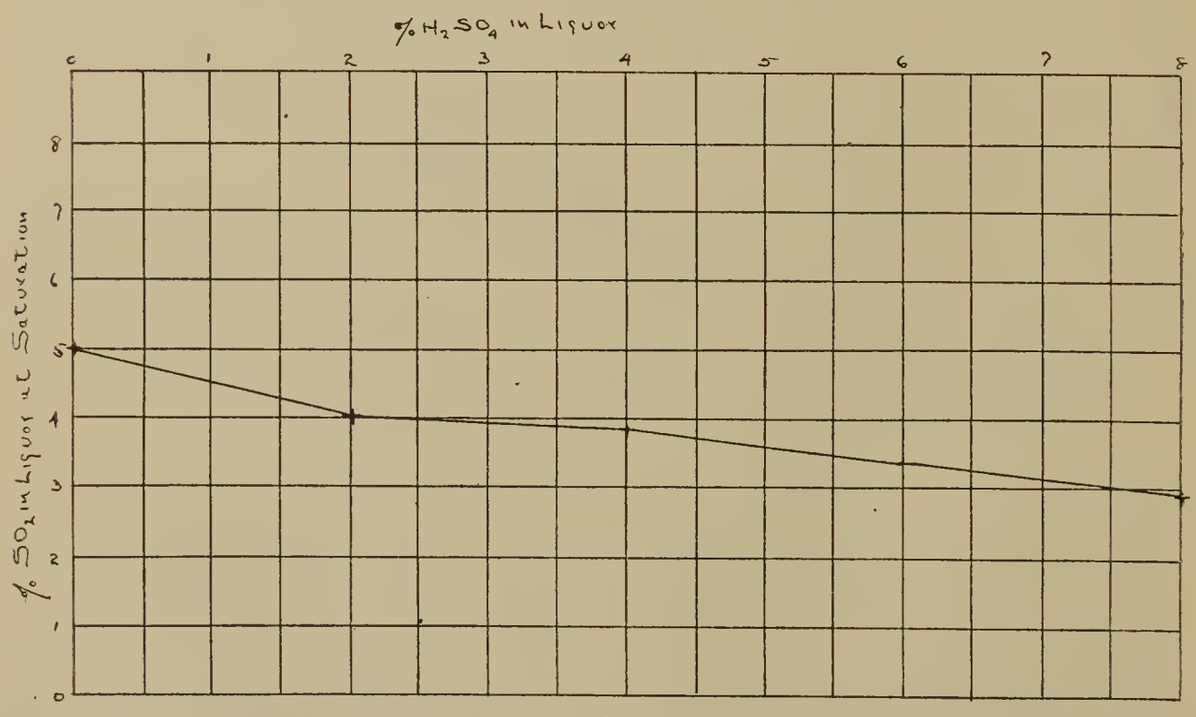
made, showing the effect of copper, iron and aluminum sulphates and free acid upon the solvent power of the liquor. It will be noted that the first two have but little effect, while the last two diminish markedly the amount of gas which can be dissolved. Supposedly 100 percent gas was used in these tests. Fig. 26 shows the actual absorption obtained in practice, using a roaster gas in a tower some six feet (1.8 m.) in diameter and twenty-five feet (7.5 m.) high, packed with coke. In general it will be seen that we cannot hope to get more than a maximum of 0.2 percent free SO_2 by analysis in electrolyte under operating

conditions, unless compression of the roaster gas is resorted to. The furnace used was an ordinary six hearth, eighteen foot



Liquor: 4 percent H_2SO_4, 0.2 percent Fe'''; 70° F. (21° C.)

FIG. 24. Effect of Various Sulphates Upon Solubility of SO_2.



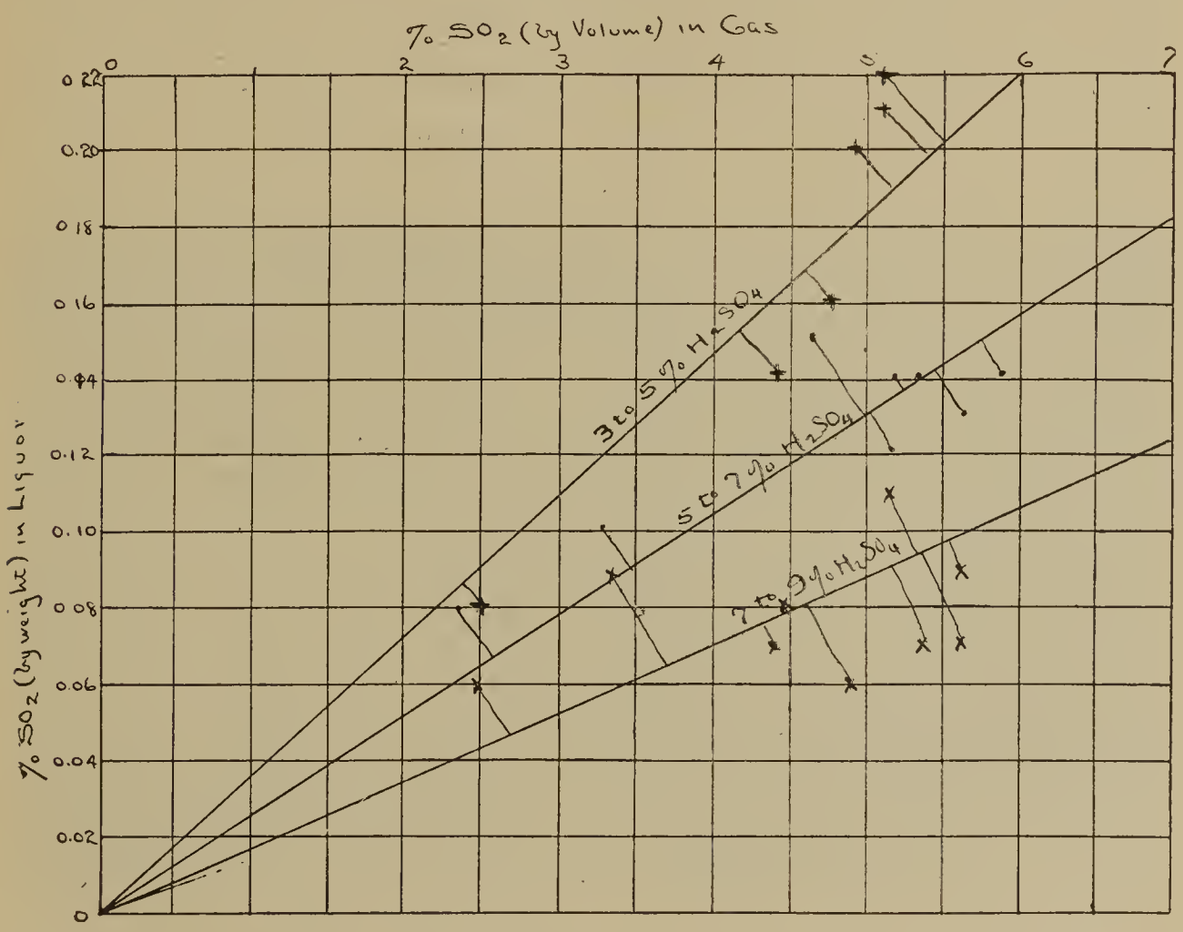
Liquor: 0.2 percent Fe''', 3 percent Cu, 3 percent Fe'', 3 percent Al_2O_3; 62° F. (17° C.)

FIG. 25. Effect of Free Acid Upon Solubility of SO_2.

(5.4 m.) MacDougall, arranged for metallurgical work, sending gases to waste so that 6 percent SO_2 by volume was the maximum richness of gas obtainable.

We have three available reducing agents for ferric sulphate—sulphur dioxide, cement copper and the calcines leached as a source of copper.

For complete reduction, about 0.5 unit of sulphur as SO_2 is required for each unit of copper deposited, the iron sulphate acting as a carrier of oxygen from the anode to the SO_2 tower. As copper-bearing sulphide minerals generally carry about 2 units of sulphur per unit of copper, we have a margin of 75



Liquor about 3 percent Cu, 2.5 percent Fe'', 0.3 percent Fe''', 3.7 percent Al_2O_3; 85° F. (29° C.)

FIG. 26. SO_2 Absorbed from Roaster Gas in Practice.

percent of the sulphur contents to cover losses in calcines, escaping tower gases and free SO_2 absorbed but later blown out of the liquors. The 0.5 unit utilized will add approximately 1.5 units free sulphuric acid to the system, which represents the amount of acid which would have to be run away in purifying the electrolyte were SO_2 the sole source of reduction utilized.

There are several difficulties involved in the use of sulphur dioxide as a reducing agent, aside from the impossibility of

obtaining a concentration stronger than 0.15 to 0.20 percent in the liquors. When an acidified solution of ferrous sulphate is made up, it is a very pale green in color. Copper sulphate added to this at once masks this green entirely and the liquor appears a true blue. When this liquor is oxidized by anodic oxygen or by hydrogen peroxide, for example, the ferric sulphate formed turns it a bluish green. Now when SO_2 is bubbled through, it would be expected that the original blue would be restored, but unless the liquor is quite warm this is not the case and if the liquor is hot the amount of gas absorbed is so small that but a small amount of reduction will exhaust its power. In a cool liquor the SO_2 turns the liquor a brilliant grass green and it requires either heating to about 160° F. (71° C.) or a period of rest of some 16 hours to restore the blue color indicative of complete reduction. Neither of these methods are commercially practicable and the way of escape appears to be to use warm liquors, circulating them through the cells at such a rate that but about 0.1 percent Fe is oxidized in transit, which small quantity a very small amount of free SO_2 seems capable of quickly reducing.

The next step is to use a certain proportion of cement copper as a reducing agent after the liquor leaves the tower. This not only readily reduces any traces of ferric iron or partial reduction compounds remaining, but precipitates any chlorides as cuprous chloride as well. Whatever iron, alumina or other impurities are dissolved from the calcines in leaching will have to be removed by systematic withdrawals of electrolyte which can be cemented upon iron. Perhaps 15 percent of the copper leached will pass through this channel, and the method proposed forms an easy way of converting it to cathode copper.

The calcines to be leached are a fairly effective reducing agent for ferric sulphate, and at least half of the ferric iron contents of a liquor are reduced when passed through the leaching plant.

EFFICIENCIES.

We are interested in four efficiencies:

(1) *Current Efficiency at Cathodes.*

(2) *Quality of Cathode.*

(3) *Efficiency of Oxidation at Anode.*

(4) *Sulphur Efficiency.*

Current Efficiency at Cathode.

About fifty separate runs were made in the cells shown in Fig. 3, during which some four tons of cathodes were deposited. The anodes shown in Fig. 6 were held rigidly in place on the cells, eight anodes and seven pairs of cathodes being used in each cell. In most of the work the liquor was circulated through four cells in series. The cathodes shown in Fig. 27 were freely suspended from their supporting bars by hooks made from insulated wire, but spacing blocks were so arranged that when the cathodes rocked under the influence of the compressed air agitation employed, they could not touch the anodes and cause

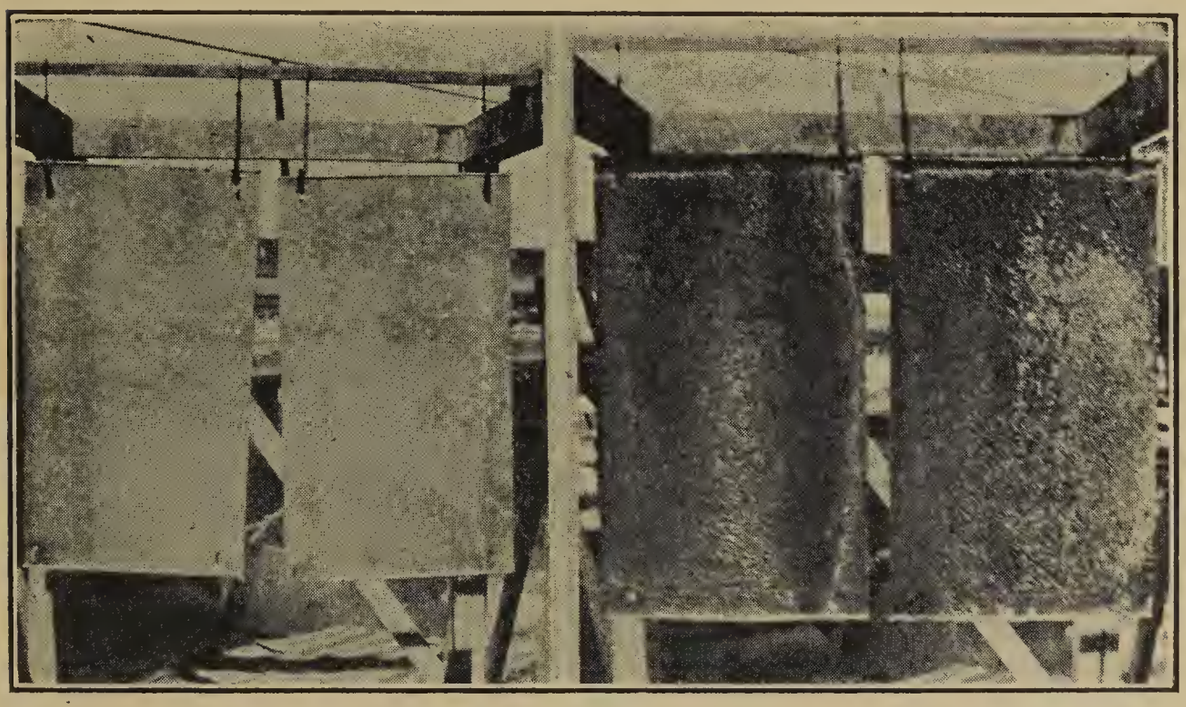


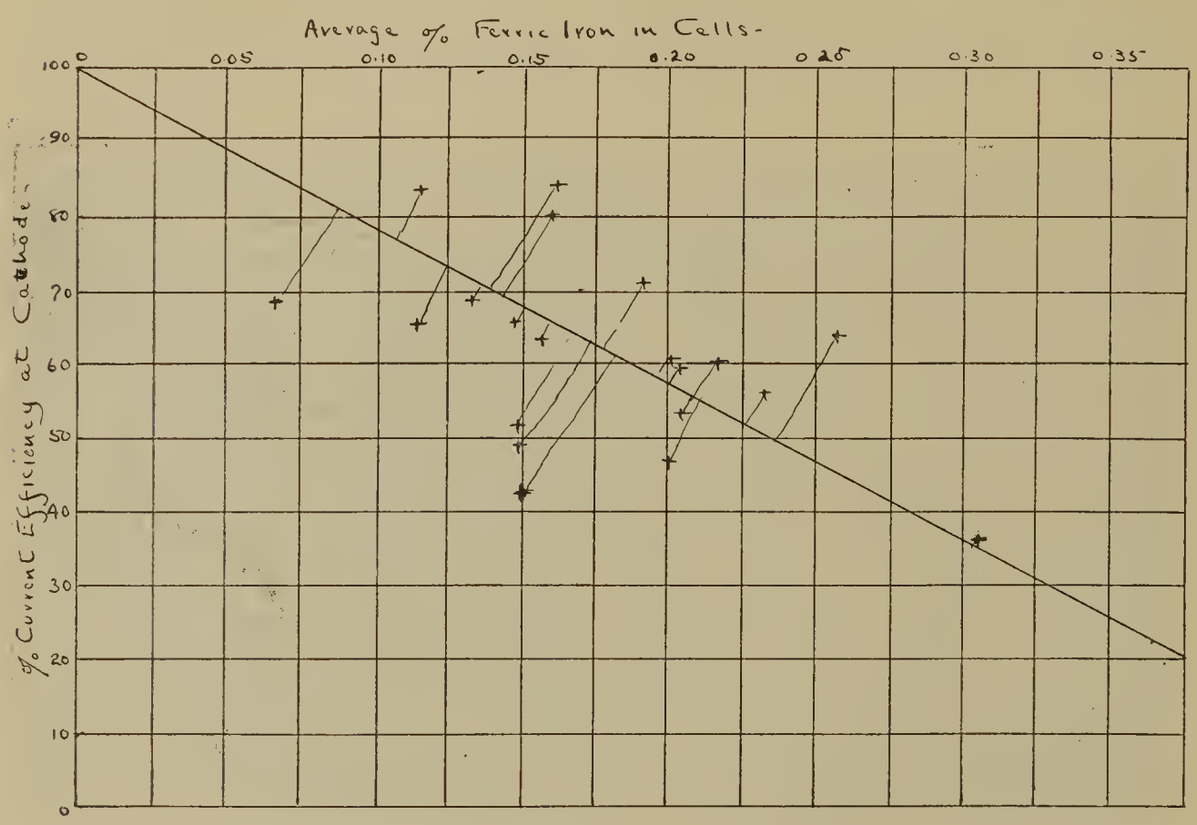
FIG. 27. Smooth Cathodes. FIG. 28. Furrowed Cathodes.

short circuits. As mechanical short circuits were supposedly impossible and as the agitation resulted in a beautifully smooth deposit without any tendency to form trees, we will assume that any deficiency from 100 percent current efficiency at the cathode was due to redissolving of the copper by ferric sulphate formed at the anode.

We have six factors influencing the rate of corrosion at the cathode: the concentration of ferric sulphate in the electrolyte, the temperature of the electrolyte, the concentration of aluminum sulphate in the electrolyte, the efficiency of contact with the

cathode due to agitation, the surface exposed to corrosion and the offsetting effect of the rate of deposit, or, in other words, current density.

The influence of the first of these factors, the concentration of ferric sulphate, under operating conditions, is shown in Fig. 29, where the average of the ferric sulphate entering and leaving the cells in the large scale runs is plotted against the current efficiency obtained. The existence of other variables scatters the points more or less, but the relationship is clearly indicated.



Liquor about 5 percent H_2SO_4, 3 percent Cu, 2.5 percent Fe'', 3.7 percent Al_2O_3; 118° F. (48° C.)

FIG. 29. Effect of Ferric Sulphate Upon Current Efficiency in Practice.

The temperature of the electrolyte was held at about 120° F. (49° C.) entering the cells in most of the large scale runs. In the presence of aluminum sulphate the effect of temperature upon corrosion is not very marked.

The aluminum sulphate was consistently held above 3 percent and in general the protective relationship established in the small tests was verified.

The rate of agitation employed was determined entirely by the voltmeter readings. The higher the alumina the greater the

agitation called for and a limit around 4 percent Al_2O_3 was reached where the cells foamed badly.

The surface exposed to corrosion enters in rather an unexpected way. As long as the current efficiency is 65 percent or over, the corrosion seems quite uniform and the cathode remains relatively smooth. Below this efficiency, however, the corrosion cuts grooves or furrows in the cathodes. These furrows present increased surface to corrosion and an unstable condition ensues which causes the efficiency to fall day by day until a very low value is reached. The difference in appearance between cathodes which have been operating above and below this critical value is shown in Figs. 27 and 28.

The current density in the large scale runs was held at 13 amperes per square foot (143 per sq. m.) because it was found difficult to obtain thorough depolarization at higher rates.

Quality of Cathode.

Physically, most beautiful cathodes were made when the rate of corrosion was properly controlled. This was, of course, due to the burnishing effect of the agitation in the cells. Chemically, three possibilities have to be considered—fouling by cuprous chloride, contamination by copper sulphide and plating out of arsenic, etc.

Cuprous chloride is purely a local problem where the water supply or the calcines carry chlorides and the use of cement copper appears to be an adequate remedy. Some cathodes made without the use of cement, analyzed 2.9 percent Cl, while others made where cement was used, showed 0.4 percent Cl, indicating that a more thorough use of the cement would eliminate the cuprous chloride without difficulty. This same problem is being handled at Chuquicamata by precipitating upon shot copper.

The proper reduction of ferric sulphate by sulphur dioxide will not leave partial compounds which blacken the cathodes. While some of the earlier copper showed the presence of sulphur, the later runs gave out 0.002 to 0.003 percent.

Small scale experiments, using an electrolyte to which 1 percent arsenic as As_2O_3 had been added, yielded cathodes running but 0.0011 percent As.

Anode Efficiency.

The anode efficiency was ascertained for 27 of the large scale runs, as follows:

The theoretical oxidation of ferrous sulphate was calculated from the cell—ampere—hours for each run. The gain in ferric sulphate was then figured from the quantity of liquor circulated and the shaking machine determinations on the entering and leaving liquors. To this was added the quantity of ferric iron reduced at the cathode as shown by the current efficiency, the sum being the iron actually oxidized electrolytically at the anode and chemically by the air used in agitation. The results ran in general from 90 to 115 percent. Some runs, to determine the amount of oxidation due to the air, indicated perhaps 15 percent, so that the depolarization was apparently perfect.

Sulphur Efficiency.

We have available, in general, 2 units of sulphur per unit of copper. We lose perhaps 10 percent in the calcines and some, let us say another 10 percent, must be lost in the exhausted tower gases. We have an anode efficiency of oxidation of say 110 percent, including that due to the agitation. This will call for 0.55 unit sulphur per unit of copper, in the form of SO_2, to reduce the equivalent ferric sulphate. We have, therefore:

Lost in Calcines,	0.20	unit
Lost in Tower Gases,	0.20	"
Used in Reduction,	0.55	"
	0.95	"
Total Available,	2.00	"
Possible Loss in Liquor,	1.05	" S per unit Cu.

If we assume 0.15 percent free SO_2 in liquor leaving the tower, this 1.05 units will supply 700 units of liquor. We must, therefore, remove 1 unit of copper by deposition from 700 units, or less, of liquor. This corresponds to an oxidation of 1.77 units of iron, or 0.25 percent increase in ferric iron in passing through the cells. This comes within the danger limit shown by Fig. 29.

If we wish to run at lower ferric iron increase we must recover some of the free excess SO_2 in the liquor and use it again in a secondary tower, or figure on less than 0.15 percent in the liquor leaving the tower.

CONCLUSIONS.

Carbon anodes will stand up in sulphate liquors if they are properly depolarized.

Aluminum sulphate can be used as a substitute for a diaphragm.

2.25 lb. (1.019 kg.) of copper per K.W.H. can be recovered under proper operating conditions.

Great quantities of various sulphates present as impurities do not foul the cathodes.

Three or possibly 3.25 units of acid are made per unit of copper, of which 1.5 to 1.75 units are new acid from the tower gases.

No mechanical difficulties are experienced in the tower, but a thorough study remains to be made of the chemistry of reduction of ferric sulphate by sulphur dioxide in order to utilize the roaster gas to best advantage.

DISCUSSION.

Chairman L. D. Ricketts: Gentlemen, I do not think that we can overestimate the importance of these two papers. In the Southwest we have stored up millions of tons of tailings in which the copper exists partly as sulphide and partly in an oxidized condition. Mr. Addicks' first paper suggests a likely process for the treatment of such material. His second paper deals with the recovery of copper from clear solutions of notable strength, and such solutions may come from the sulphating roast or direct from the leaching of completely oxidized copper ores of which vast deposits are known to exist.

What strikes me particularly about the latter paper is the keen perception shown and the clear manner in which the writer has attacked the fundamental principles of the process. He calls your attention to the fact that ferrous sulphate is necessary in the electrolyte and is an ideal depolarizer; that sulphurous acid

must be used to reduce the ferric sulphate produced and thus prevent re-solution of copper at the cathode; that mechanical agitation in the cell, in order to bring the ferrous sulphate in contact with the anode and the copper in contact with the cathode, is essential to efficient work; that lead anodes are undesirable because they do not permit complete depolarization, and that carbon anodes are ideal for the purpose. When the ferric salts were kept low by the use of sulphurous acid there was no trouble during the life of his experiments from softening and deterioration.

E. H. Hamilton: Does sulphuric acid accumulate? I was wondering whether Mr. Addicks found the acid accumulated or not.

President L. Addicks: That is a relative question. We had so much alumina in the ore, and the rate of neutralization was so high, it was more a question of getting enough acid than too much. You have raised a large question there. In the process we were attempting we are bound to get whatever acid equivalent there is in liquors contaminated with other things where it is of no use. If we have any acid that is left over, there is no market for it, consequently no revenue derived from it, which is the whole question.

F. Laist: Mr. Addicks spoke of the difficulty of getting a strong solution of SO_2 from a weak gas, such as would be encountered in practice. I believe Dr. Ricketts mentioned that point yesterday in connection with the paper he presented on some problems in copper leaching. I think it might be of interest to give a brief outline of some of the experiments we made in Anaconda in the course of the past year and a half, on the precipitation of copper from cupric chloride solutions by means of SO_2. While the plan decided on for our tailings treatment uses scrap iron as a precipitant, we wished to make sure that that really would be the best method. Among other methods investigated was the old Hunt and Douglas method, which consists of adding to the copper sulphate solution sufficient common salt to chloridize the copper. The copper is then precipitated by SO_2 gas in the form of cuprous chloride, which is a white insoluble precipitate containing about sixty-five percent copper.

We carried the process on in two stages. First, we dissolved sufficient SO_2 gas in the solution. Second, we heated the resulting liquor to 90° C., which caused reduction of cupric to cuprous chloride. The latter separated out in cooling. Our solution contained about 1.5 percent copper and required about 0.7 percent SO_2 for precipitation. We found it impossible to dissolve over 0.2 percent at atmospheric pressure when a 10 percent gas was used. After we started using a closed tank for the work and forced the gas in under a pressure of about 15 lb. per sq. in. (1 kg. per sq. cm.) we obtained the desired saturation without trouble. There was no trouble about getting a 10 percent gas from the furnace, although it was necessary to take the gas from the second floor in order to avoid admixture of air, entering through the feed openings. With suitable apparatus 80 percent of the SO_2, or better, could be absorbed.

The point I wish specially to call attention to is the greatly increased strength of solution which it is possible to get from a weak gas by the use of moderate pressures.

President Addicks: I have never had any difficulty with the absorption towers, nor did we have any difficulty in getting as much gas absorbed as we did in the laboratory. We put in a stand-pipe, forty or fifty feet high, and let the liquor run through that, and we got absolute absorption of SO_2. While we did not get any increase in efficiency, we got what we had a right to expect from the increased pressure.

Mr. Hamilton: The electrolysis of the chloride solution works well in the laboratory, but it has not been a success commercially so far.

Chairman Ricketts: I am not familiar with processes calling for electrolytic recovery of copper from solutions containing chlorine salts. But I believe chlorine has a bad reputation in such work.

Chas. Butters: I would like to ask Mr. Addicks, in reference to carbon anodes and the use of them as depolarizing anodes in a cyanide solution, whether they soften?

President Addicks: With chloride electrolysis there has never been any difficulty. Chlorine has no oxidizing effect on the car-

bon. As you are running at low efficiency, you are liberating a great deal of oxygen, however, in cyanide work.

Mr. Butters: That is one of the reasons why we threw out electrolytic precipitation of gold and silver. We got no efficiency. We were never able to get an anode where we got over two or three percent efficiency.

President Addicks: You must take care of the product of depolarization. You absorb oxygen at the anode by putting in some other product, and you must do something with that in the end.

Chairman Ricketts: I wish to say, as far as Mr. Addicks' first paper is concerned, that in the Southwest we have porphyries that have been subjected to intense chemical action and contain a great deal of clay. In the old days when we used to crush to 1.5 mm., fully fifty percent of the product would pass a two-hundred-mesh screen. I think such ores would give a great deal of difficulty in leaching, even after a sulphating roast, if an attempt were made to gain a strong solution of sulphate of copper, but possibly we might make the process successful if we used a large amount of solution and produced a solution weak in copper from which the copper would be recovered with scrap iron and metallized calcine. Though such a method of recovery of copper from solution is comparatively expensive, the metal would be obtained very profitably because the material to be treated is tailings that are already mined and sized and that are comparatively rich.

Referring to Mr. Addicks' second paper, and especially referring to the use of sulphurous acid to reduce the ferric iron produced by depolarization, at plants located at points like Douglas, Arizona, where immense amounts of sulphur are going to waste as sulphurous acid gas, the question of efficiency does not enter in the problem. In certain districts in the Southwest, especially at Ajo and Globe, Arizona, we would have to consider the importation of pyrite or sulphur for the manufacture of the sulphurous acid gas. In such cases the question of complete absorption becomes very important, yet complete absorption of the gas as produced by burning sulphur or pyrite presents many difficulties. In our experiments we did not get very good absorption

in a coke tower. The solution possibly followed channels. At all events we found if we could spread out the liquid in very thin sheets over large surfaces we obtained much greater absorption. We also found that a neutral solution absorbs more gas than an acid solution. Where, however, complete absorption is important, it occurs to me that the pumping cost will be considerable and the cost of the construction of the necessary absorption towers will be very great.

Mr. Addicks' paper calls attention to the fact that if solutions containing ferric salt and sulphurous acid are heated to about 130° F. (54° C.), the reduction is almost instantaneous. I think the question of obtaining a pure gas is important. If by some cheap method 100 percent sulphurous acid gas could be obtained, the necessary amount could be pumped under a low pressure into the warm solutions and the reduction might be instantaneous and the cost, both of operation and for construction, might be very considerably lessened.

G. D. VAN ARSDALE (*Communicated*): The present status of leaching and electrolysis of copper ores reminds one decidedly of the surgical bulletin that the operation was successful, but the patient died. Those of us who have worked on this problem have practically demonstrated our proposition, but are now under the necessity of something of a struggle to keep the process alive against the competition of flotation, which under anything like equal conditions will win out on account of the great difference in installation costs in its favor. Leaching will, accordingly, have a chance only in cases where a sufficiently higher extraction can be shown in its favor, for example with ores carrying appreciable amounts of oxides or otherwise not adapted to yield high extraction percentages by the present flotation methods.

Mr. Addicks' description of the results of the experiments during the past year on electrolysis at Douglas is interesting, but there are several points contained in the paper which I would like to discuss both for the sake of clearing up possible misunderstanding, and also because I feel that some of his conclusions are to a certain extent matters of opinion. This may be permitted, as I was in charge of the original tests, and am now supervising the close of the present series, and since I recommended the gen-

eral scheme finally adopted as the result of my research work in New York and at Douglas.

The original experiments were started with the idea of using SO_2 as the principal depolarizer, although it was recognized that any leaching solutions would carry both iron and alumina. These experiments may be considered as fairly successful, since a yield of about 2 lb. (0.9 kg.) of copper per K. W. H. was obtained under proper conditions, at commercial current density.

It was found, however, by later laboratory research, that much better results could be obtained by the combination of ferrous iron and SO_2 than by either alone, and that the effect of alumina was favorable in that higher cathode efficiencies could be obtained when it was present. As a result of this work I therefore recommended an electrolyte high in iron, high in alumina, and the use of sufficient SO_2 to reduce any ferric iron originally present and to reduce the ferric iron as produced. Plans were also made and a tower installed for doing the major part of the absorption and reduction by SO_2 outside of the cell-room. Naturally some difference of opinion as to details of application of this general scheme developed; the matter of the entire exclusion of SO_2 from the tank-room being one of these, which I still believe has not been fully settled.

It is of course true that when SO_2 is used without ventilation the tank-room atmosphere is unbearable, but the main reason for making the principal absorption in a tower rather than in the cells is the fact that with a limited supply of SO_2 it becomes necessary to secure an efficient absorption, and blowing dilute SO_2 through cells is not an efficient absorption arrangement, while a properly built and run tower is efficient.

In actual work it will be difficult to have an electrolyte free from SO_2, even if no SO_2 is purposely introduced into the cell-room, unless the liquors are freed from such excess SO_2 before entering the cells, which would be difficult and wasteful, as there is no possible way of recovering economically this excess gas.

The tank-room operation therefore becomes a question of blowing air through solutions carrying appreciable amounts of SO_2, or the original scheme of using SO_2 seems to show that unless special means are adopted to get rid of this excess SO_2, that there will be little to choose from in the way of cell-room

atmosphere for either method. In other words, it seems certain that it will be necessary to install positive ventilation in either case, and granting this it seems decidedly more reasonable to use a reducing gas rather than air as a means of agitation, especially for warm solutions, since in this way the oxidation produced by the air, which is a very respectable percentage of the total, can be entirely avoided. This would probably mean handling cathodes by hand instead of mechanically, but as the largest refinery in the country does this, this will probably not prove a serious matter. The exit gases from the absorbing tower, working at say 50 percent absorption, may be used for this purpose and a clean gas secured, with practically no excess amount needed.

Regarding Mr. Addicks' explanation of the prevention of anode disintegration, both his and my own theory of this naturally agree that this is due to the inhibition of oxygen evolution by the depolarizer present. My own idea regarding the disintegration which occurs when oxygen is evolved is that this is due to the mechanical disrupting action of the bubbles of gas in the pores of the carbon. I simply give this as an alternative to the idea that something akin to ozone is formed, which acts on the carbon or on its more or less carbonized binding material, thus breaking down the anode. Both of these are matters of opinion, and the important fact of course is that some of the original pieces of graphite which I bought at the start of the experiments are still in good condition, having withstood very rough usage, although before the start of this work graphite was generally stated, even by the makers, to be totally unsuited for sulphate electrolysis.

Mr. Addicks' reasoning in support of his theory does not, however, seem entirely clear, as it is known that graphite anodes in chloride solutions will disintegrate as a result of the evolved chlorine, although more slowly than in sulphate solutions. I believe it is true also that in the process of graphitization, the small amount of binder becomes completely graphitized, and that the result must be looked on as very nearly pure and uniform graphite, instead of a "carbon conglomerate." Further, I take it that the statement that "oxygen liberated ..... at a lead anode gives but partial response" means that the anode oxidation efficiency for ferrous iron with lead anodes is low.

This is true, but it is not necessary to assume any different properties of the oxygen evolved in the two cases, or that something akin to ozone is produced, since the much more simple and obvious explanation is that with the lead anodes a part of the evolved oxygen is used up in oxidizing ferrous iron, and a considerable part in peroxidizing the lead, thus accounting for the lower oxidation efficiency for ferrous iron. Since also graphite is comparatively inert to oxidizing agents in the wet way, it does not seem probable that there is any chemical action of the evolved gases, in view of the fact that the graphite in its finished form, as used, contains no binding agent, these being either volatilized or graphitized during the manufacture, and also since there is no evidence of anything akin to ozone being formed.

While it is very improbable that SO_2 alone as a depolarizer will be used in practical work, I would like to correct a possible misunderstanding of the statement at the top of page 80 of Mr. Addicks' article. It is of course true that in large-scale work with insufficient SO_2 or ferrous iron, there will be softening of the anodes, nevertheless work done on the large scale with solutions containing at the start no iron, and only a comparatively small amount later, showed that the amount of SO_2 that could be introduced from furnace gases into such liquors was sufficient to prevent entirely disintegation. In other words the nature of the depolarizer is immaterial with respect to disintegration, provided enough is present to inhibit oxygen evolution. It is also possible to introduce enough SO_2 from furnace gases into an electrolyte to obtain a very satisfactory depolarization, although, as brought out by Mr. Addicks, the amount that can be absorbed depends on the composition of the solutions to a considerable degree. With a solution containing excessive amounts of copper, iron, and aluminum sulphates and free sulphuric acid, about 15 percent SO_2 is nearly the maximum that can be obtained from roaster gases running say 4 to 6 percent SO_2, without compression. While such heavy solutions may perhaps be considered best from the standpoint of electrolysis alone, the conditions imposed by leaching limit the strength and composition of the electrolyte, and tests show that liquors containing anything like such amounts of salts will be impracticable for any ordinary leaching problem, on account of their great tendency to crystallize out,

especially in colder weather, the use of steam being prohibitive for heating under Southwestern conditions. From a leaching standpoint, generally speaking, more dilute liquors are also desirable in that less installation for washing is required, and there is less volume of wash liquors, and less copper locked up in the system.

With more dilute solutions, the amount of SO_2 that can be absorbed from furnace gases will be sufficient for it to act as a "chemical diaphragm," and since we have seen that cell-room ventilation will probably be required in any case, its use in this way may be considered, and in my opinion will prove preferable to the alternative plan of depending on alumina as the chemical diaphragm, since the amount of the latter, to be very effectual, will be beyond a practicable amount from the leaching standpoint. The proper composition of the liquors is a very complicated problem, requiring careful balancing for any particular case, since not only in the electrolysis do we have several more variables than in ordinary copper refining, but also an entirely separate set of conditions in the leaching, imposing limitations in turn.

If we assume 2 lb. (0.9 kg.) Cu per K. W. H. as a minimum commercial yield, it is safe to say that this yield can be obtained from practically any solution composition likely to be obtained, and under favorable conditions much higher, 3.16 lb. (1.43 kg.) being the maximum obtained in recent work at 13 amperes per square foot (1.4 amperes per square decimeter), and cathode efficiency of a little over 90 percent, under possible commercial conditions.

Regarding the question of the character of the deposited copper, in my opinion it is not yet safe to say that cathode copper equal to electrolytic can be obtained under all conditions of electrolyte composition, although I believe it is safe to say that under normal conditions with any of the ores leached so far there will be no cathode constituents that will not be eliminated during the operation of melting, poling, etc., of the cathodes, previous to casting.

The purity of the deposited copper will probably be more or less inversely proportional to the percentages of salts other than copper in the electrolyte. This is clearly shown by the following

analysis of representative samples of cathodes made under different conditions in this respect.

	1	2	3
Cu.	99.91	96.75	99.45
As.	0.0003	0.031	0.037
Sb.	0.0013	0.005	0.003
Fe.	not det.	0.012	0.007
S.	not det.	0.003	0.002
Cl.	not det.	2.93	0.34

Sample No. 1 is from a quantity made from an electrolyte of average composition about 1.5 percent Cu, 0.5 percent H_2SO_4, 0.5 percent Fe, and 0.25 percent Al_2O_3. For samples No. 2 and No. 3 the electrolyte composition was about 3 percent Cu, 3 percent Fe, 5 percent H_2SO_4, and 3 percent Al_2O_3. In the electrolyte for sample No. 1 the SO_2 content was about 0.6 percent; for the other samples the SO_2 content was practically *nil* during electrolysis. The arsenic content of samples 2 and 3 was traced to impure sulphuric acid used for leaching carrying 0.37 percent As. The present electrolyte carries only traces of As and Sb.

Regarding chlorine, unless, as at Chuquicamata, this comes from the ore, it seems probable that the amount introduced by any water supply of reasonable purity will be balanced by that carried away by the tailings and in any solution sent over scrap iron.

Regarding the durability of the anodes, these have apparently resisted disintegration, since some of the original lot are still in use and in good condition. A careful determination has recently been made on this point. All of the anodes in two cells, after running for a considerable time, were carefully scraped until the original graphite surface was restored, and the graphite removed by the scraping dried and weighed. Compared with the weight of copper deposited during the period, the anode loss proved to be entirely negligible, and since such scraping is a much more drastic treatment than any likely to be encountered in practice, it seems safe to say that the durability question is definitely settled.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, at a Joint Session with the American Institute of Mining Engineers, in San Francisco, September 17, 1915, President L. Addicks in the Chair.

SOLUTION STRATIFICATION AS AN AID IN THE PURIFICATION OF ELECTROLYTES.

By Francis R. Pyne.

In the electrolytic refining of copper there are two attendant evils of special prominence. One is the tendency of the electrolyte to stratify or form layers of various compositions, and the other is the accumulation of impurities in the electrolyte.

The stratification is caused by the formation of a heavy solution at the surface of the anode owing to the solution of copper, and by the formation of a lighter solution at the cathode owing to the plating out of copper. Unless the degree of stratification is greatly impeded, the result will be a very unsatisfactory cathode deposit, which will be at best heavy and lumpy at the bottom, while mealy and of poor quality at the top. The greater part of the current will pass through the strata of highest concentration, causing frequent short circuits and uneven dissolving action at the anode, with all the attendant deposition troubles.

As a preventive, the electrolyte is circulated throughout the tanks at a rate which varies with local conditions at each plant. Too rapid a circulation is liable to carry slime, if present, to the cathode, fouling it and causing metal losses in silver and gold. Too slow a circulation does not sufficiently suppress the stratification. Where the current density is high the circulation must be more rapid than would be the case with a lower density.

To show the degree to which stratification will take place, the following figures are taken from a paper by Mr. W. T. Burns on "The Great Falls Electrolytic Plant" (Trans. A. I. Mining Eng., August, 1913). This illustration is selected on account of the high current density in use at Great Falls, 36 amperes per square foot (400 per sq. m.), which is conducive to very marked stratification. Samples of the electrolyte were taken between the

center pair of electrodes at the following levels below the solution line: Zone 1, 6 inches (15 cm.); Zone 2, 17 inches (43 cm.); Zone 3, 28 inches (70 cm.); Zone 4, 39 inches (100 cm.).

The figures represent the average of 104 samples taken during seven consecutive days, and the results are reported in grams per liter.

Circulation at the rate of 6 gal. (23 liters) per minute.

Zone	Sp. Gr.	Acid	Copper
1	1.213	174	38.4
2	1.216	172	39.2
3	1.216	171	40.2
4	1.228	153	49.9

Circulation at the rate of 4 gal. (15 liters) per minute.

Zone	Sp. Gr.	Acid	Copper
1	1.211	163	40.0
2	1.214	161	41.1
3	1.216	159	42.0
4	1.263	139	67.8

Circulation at the rate of 2 gal. (7.6 liters) per minute.

Zone	Sp. Gr.	Acid	Copper
1	1.210	167	37.8
2	1.213	165	39.0
3	1.217	162	41.0
4	1.265	146	66.4

Circulation shut off for seven hours.

Zone	Sp. Gr.	Acid	Copper
1	1.185	179	23.4
2	1.210	164	38.0
3	1.230	151	51.8
4	1.255	138	65.5

The above figures clearly show the increase in stratification with decrease in circulation.

Regarding the accumulation of impurities in the electrolyte, these impurities are present in the anode, whence they pass into solution through the action of the current, or they may come from some outside source, for example, an addition agent. If allowed to accumulate in the electrolyte without restraint they may foul the cathode by being deposited thereon either electrically or mechanically. They may also increase the resistance of the electrolyte causing thereby a loss of power, or they may increase the specific gravity so that the settling of the slime is

hindered, with a possible loss of slime in the cathode. In order to prevent these undesirable effects, the impurities in the electrolyte are not permitted to go above certain limits, and this is accomplished by withdrawing a certain amount of electrolyte from time to time for the removal therefrom of the undesirable constituents, and this removal must be done in such a manner that the valuable ingredients, such as copper and acid, shall not be wasted.

The customary method in use at the present time is to withdraw daily from the electrolyte a certain portion which is either worked for bluestone ($CuSO_4.5H_2O$), or else passed through tanks containing insoluble anodes. It is with the latter method that this paper deals. The treatment with insoluble anodes removes a large part of the copper from the electrolyte, but requires a large power expenditure, the output per kilowatt hour being one to two pounds (0.45 to 0.90 kg.) as against an output of eight pounds (3.63 kg.) in the regular refining tanks. Moreover the quality of the deposited copper is greatly inferior to the regular cathodes.

The solution from this first set of insoluble anode tanks is then passed through a second set, usually at a slower rate of circulation, and this second set of tanks removes the balance of the copper and practically all of the arsenic and antimony. The solution is then treated in any suitable manner for the elimination of such other impurities as may be desired.

From the above it is evident that could a solution be secured from the regular tanks sufficiently low in copper to avoid treatment in the first set of insoluble anode tanks, there would result a considerable saving in power, assuming that it contained practically an undiminished amount of impurities.

Knowing the tendency of the electrolyte to stratify, an endeavor was made to utilize this principle as a means to this end. Accordingly a tank was constructed in which the circulation was so arranged that stratification would readily occur. The electrolyte entered the tank just above the slime line and was drawn off through two outlets, one at the solution line, the other just above the slime line and opposite the inlet. (U. S. Patent No. 1,148,798).

The accompanying figure shows a sectional elevation of the tank as applied to copper refining. *AB* is the slime line, *H* the outlet for removal of slime from the tank, *CD* is the solution line. The electrodes have been omitted for the sake of clearness. The electrolyte enters the tank at *E* and is withdrawn through the upper and lower outlets, *G* and *F* respectively.

If the tank is filled with electrolyte and the upper outlet closed, any solution entering the tank through the inlet *E* will pass directly to the outlet *F* without disturbing the solution in the tank, providing the amount entering and leaving the tank is the same. If, however, the upper outlet *G* is open as well as the outlet *F*, a part of the incoming solution will flow through *F* while the remainder will rise in the tank to take the place of that withdrawn through the outlet *G*.

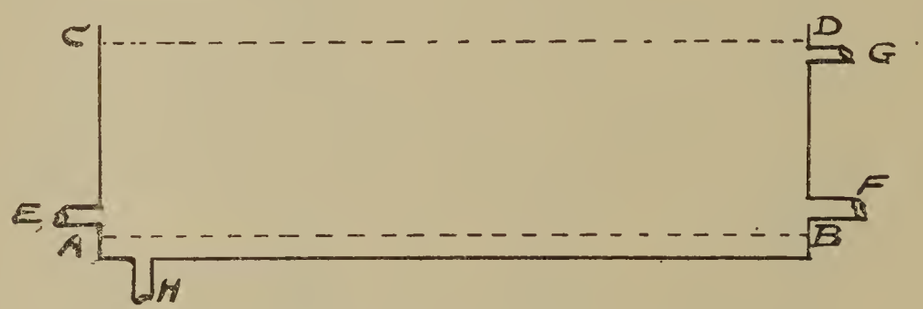


Fig. 1. Showing Diagrammatically the Tank Openings.

Now if the electrodes are in place and the normal current is passing and all circulation is stopped, the heavy solution formed at the anode by the copper passing into solution will stream downwards to the bottom of the tank, while the lighter solution at the cathode, due to the removal of the copper from solution, will rise. This is very clearly shown by the test made by Mr. Burns, in which the circulation was stopped for a period of seven hours. Therefore, there will eventually be a stratum of heavy copper solution around the lower part of the cathode, while the solution in the upper part of the tank will be very low in copper and consequently lighter. The deposit on the lower part of the cathode will be rough and heavy while that on the upper part of the cathode will be loose and mealy.

As stated before, this is a very unsatisfactory condition of affairs, and it is therefore necessary to have such a circulation that the cathode will receive a satisfactory deposit throughout.

This is accomplished by so regulating the flow from the upper and lower outlets that the heavy solution at the bottom of the tank will rise to such a height that there is a sufficient amount of copper at all points of the cathode. When proper regulation has been made, the regular tank room solution enters the tank through the inlet *E*, a solution high in copper is withdrawn from the tank through the outlet *F*, while the solution from *G* is low in copper and the cathode is in all respects similar to those drawn from the regular refining tanks.

The low grade solution withdrawn from the outlet *G* has been found in practice to be lower in copper than is usually obtained from the outlet of the first set of insoluble anode tanks mentioned above, and it is delivered directly to the second set of insoluble anode tanks for the removal of the last traces of copper.

The tanks have shown no increase in voltage over that of the regular refining tanks and there is no increase in the labor or material required in their operation. The solution withdrawn from the upper outlet can be varied through quite a range of copper content, and as it is a simple matter to equip a tank for this operation, a large or small number can be kept ready to respond to variations in the amount of solution to be withdrawn from the main circulation. They can be cut in or out at any time and in any part of the circuit, without reference to the age of the copper in the remaining tanks, which must be considered when using insoluble anode tanks unless the latter form a separate section apart from the regular refining tanks. A comparison of the two methods may be seen from the following:

Former Method.—Tank house electrolyte first passed through tanks containing insoluble anodes, to remove a portion of the copper, requiring high power consumption and giving a product of inferior quality, thence to a second set of insoluble anode tanks to remove the remainder of the copper and some of the impurities, after which the solution is treated in any desired manner.

Present Method.—Tank house electrolyte drawn directly from the special stratification tanks, requiring no increase in power and avoiding the production of inferior grades of product; thence to the final insoluble anode tanks, as above.

The net saving is therefore the operation of one set of insoluble anode tanks.

DISCUSSION.

PRESIDENT L. ADDICKS: This paper gives, in a sense, a substitute for a diaphragm. The diaphragm has always been a curse to any process, while on paper it seems to be a feasible way. In this case specific gravity is used as a method of separation. We also have Hybinette's method mentioned, and the chemical methods, which are brought out in the papers to follow, on leaching, where some chemical antidote is put in the liquor so as to reduce a product before it can attack the cathode.

W. T. BURNS (*Communicated, read by F. Laist*): I have read Mr. Pyne's paper with interest and believe that the method outlined has advantage when the electrolyte to be purified is run directly to the insoluble anode tanks, without previously being treated by concentration and crystallization, for the removal of copper, as in the practice in some plants.

In connection with Mr. Pyne's statement that "the net saving is the operation of one set of insoluble anode tanks," I would like to ask him if the saving of this group of tanks in the purifying section is not obtained, in a measure, at the expense of the liberating tanks in the tank house, that is, will it not be necessary to add more liberating tanks to take care of the heavy copper electrolyte left in the refining tanks?

If the plant is not so fortunately situated, and few are, that it can market large quantities of bluestone to advantage, the surplus copper in the electrolyte must eventually be removed by means of the insoluble anode tanks, either in the purifying section or in the tank room proper.

The regular liberating tanks, treating a solution high in copper, will of course operate at a higher efficiency and produce a better cathode than the purifying tanks, but will the saving effected by Mr. Pyne's process not be confined chiefly to these advantages?

The writer's experiments, to which Mr. Pyne refers, were made to determine the effect of the speed of flow of the electrolyte

on the physical and chemical properties of the deposited copper. Arsenic, antimony and iron determinations were made on all samples taken, and these impurities were found to be present in practically the same quantities in all the samples, consequently the same volume of electrolyte must be purified whether it be high or low in copper.

President L. Addicks: I think I can answer Mr. Burns' criticism. It is quite just what he says about the fact of the use of liberating tanks where copper is gradually increasing in the liquor due to chemical action. At Chrome they have nickel in such a quantity in the anode that the copper in the liquor does not increase.

Secretary J. W. Richards: I asked Mr. Pyne, by letter, regarding the relative amounts of impurities in the strong solution and in the weak solution, and Mr. Pyne answered that on analysis of the strong and weak solutions he found that the latter, although poor in copper, contained practically the same amount of impurities per liter as the strong solution, showing that the impurities were not concentrated with the copper. The process would be inoperative unless that were so.

F. R. Pyne (*Communicated*): With regard to Mr. Burns' comments, I would state that in connection with electrolytic copper refining there are two conditions to be met: the first, the removal of the excess copper from solution; the second, the removal of impurities from solution.

The first requires the use of insoluble anode tanks treating a solution high in copper, which circulates at fairly high speed, in order to produce good cathode copper, and the over-flow from these tanks is high in copper. Of course, if conditions are such that copper does not build up in the solution, there will be no need of these tanks.

The second condition requires the use of insoluble anode tanks treating a solution low in copper, which circulates at low speed in order to eliminate the arsenic and antimony. To obtain a solution of this nature it has been necessary to take the regular tank-room solution, either direct or from the liberating tanks, both of which are high in copper, and pass this solution through the purifying tanks. Any copper in the solution going to the

latter will be recovered either as a sludge or else as a cathode, which must be re-worked in the furnaces.

By the use of the process described in the paper, the solution going to the purifying tanks from the upper outlet is low in copper, the result being that while the same amounts of arsenic and antimony are removed, there is considerably less copper to be re-worked.

As Mr. Burns states, it would mean that the copper formerly recovered in the purifying tanks would have to be recovered in the liberating tanks, but as the latter operate at high efficiency and produce good cathodes, while the efficiency of the former is low and the product unuseable without further treatment, the economy is obvious.

Should the plant produce bluestone, the solution from the lower outlet of the new tanks, which is relatively high in copper and low in acid, could be sent to the bluestone plant and an economy effected thereby on account of the smaller amount of free acid to be neutralized.

Also, in any leaching process followed by electrolytic extraction, the double circulation will permit of keeping the solution in the tanks at a higher copper content, while weak over-flow is returned to the leaching tanks. This should result in increased ampere efficiency.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, in Joint Session with the American Institute of Electrical Engineers, September 17, 1915, President J. J. Carty (A. I. E. E.) in the Chair.

TREATMENT OF SILVER FURNACE FUME BY THE COTTRELL PROCESS.

By Charles H. Aldrich.

The problem of condensation or agglomeration of the very minute particles constituting metallurgical fume has, until within recent years, furnished a problem very difficult of solution. It is, however, in many cases, extremely important, both as to its bearing upon the health of the community and upon the valuable products which may be recovered by the operation.

In the past, many tons of valuable materials have been lost through volatilization and dissipation with furnace gases, and, although the subject of metallurgical fume has received a great deal of attention of late, yet there is no doubt that in many instances fume losses are occurring daily that are entirely unsuspected by those in charge of the operations.

It has often been assumed that because the dust deposited at the end of a long flue system amounts to very little, no large amount of values pass out of the stack, and the important points that fume as well as dust may carry large values and that they present problems that demand individual treatment, are lost sight of.

During the past four years considerable work has been done at the Raritan Copper Works on treatment of gases from Doré refining furnaces, and we believe that we are in a position to state that the problem of the recovery of practically all metal values from these gases has been solved by the application of the Cottrell process.

Since this plant was the first one to use this process in connection with silver refining, a description of the methods used and results obtained will, perhaps, be of interest.

Prior to the year 1907 the only method in use for recovering

values from silver furnace gases was a system of brick flues, about 12 square feet (1 sq. m.) in cross section and 250 feet (75 m.) long, leading to a brick stack 90 feet (27 m.) high.

When a large addition to the plant was constructed in 1906, the silver refinery was remodeled and enlarged, and it was decided to install a water scrubber on the end of the flue system, based on results obtained at the Baltimore Copper Smelting and Rolling Co. with a similar apparatus. This consisted of a lead-lined tank filled with water, into which dipped 336 5-inch (13 cm.) lead pipes, which projected about 5 inches (13 cm.) below the surface and communicated with a cast-iron gas chamber above. The furnace gases were drawn from the flues by means of a six-foot (1.8 m.) centrifugal blower and forced through the pipes, bubbling through the water and passing out of a lead stack connected to one end of the tank.

The results obtained with this apparatus amply justified the considerable expense involved in its installation and maintenance, and during its operation it has saved values averaging about $50.00 per day.

It seemed evident, both from the appearance of the gases passing out and from the nature of the treatment, that no dust could be escaping, and for some time it was thought that no values of importance were being lost; the escaping cloud being apparently mostly steam. However, it was observed that if a metal sheet was suspended in the gases a deposit would form upon it which often carried several hundred ounces of silver per ton.

Early in 1911 tests were started to determine the advisability of constructing a settling flue through which the gases could be passed after leaving the scrubber and not until then was the true nature of the fume or the importance of its recovery realized.

It was found that, as had been supposed, practically all dust had been removed from the gases by the scrubber, the material remaining all being in the form of particles so fine that they formed a fog, which, when placed in a closed vessel, required from two and a half to three hours to clear up. Obviously, no practical settling flue could be constructed to accomplish this. Violent agitation with water, it was found, would clear up the gas.

Accordingly, the installation of various mechanical gas-washers was considered. The problem of acid proofing appeared serious and, as these gases contained large proportions of nitric and sulphuric acids, it will be seen that this was of importance.

A device in which the gases were to be forced through a series of lead screens in contact with running water appeared to be the most practical, and some working drawings of this were made. There were many points about this, however, which were not satisfactory. Consequently, when Dr. Cottrell's paper upon "The Electrical Precipitation of Suspended Particles" appeared in the *Journal of Industrial and Engineering Chemistry,* August, 1911, it seemed likely that the process described would perhaps accomplish the desired result upon our gases. Dr. Cottrell was communicated with and shortly after arrangements were made with him to conduct tests and, if favorable results were obtained, to construct a treater of sufficient capacity to handle the gases.

Electrical apparatus for converting 220-volt direct current up to about 45,000 volt D. C. was obtained, and during the summer of 1912 a series of tests were conducted by Mr. Linn Bradley, representing the Research Corporation, and the writer, which gave such encouraging results that it was decided to go ahead with the construction of the treater.

With regard to the details of these tests, little need be said. Briefly, the method used was the aspiration of a definite proportion of the gases, measured by a Pitot tube, through a treater composed of a 10-foot (3 m.) length of 6-inch (5 cm.) pipe provided with a central electrode of No. 20 (0.8 mm.) copper or iron wire. Clearance was determined by aspirating equal volumes of gases simultaneously through Brady filters, located at the inlet and outlet ends of the treater pipe, and assaying the filter thimbles for silver and gold.

The electrical apparatus used in the preliminary work was far from practical. It was designed for X-ray work and included a multiplicity of condensers and inductance coils together with a transformer impregnated with beeswax but without provision for cooling; consequently, as might be expected, a large proportion of time was occupied in repairing punctured con-

denser plates and scooping up the beeswax that ran out of the transformer.

The electrical apparatus finally secured for the commercial treater, which has now been running continuously for nearly two years, consisted of a 3-K.W., 220-volt, D.C., to 154-volt A.C., 60 cycle, "Hill" rotary converter, a 7.5-K.W., 154-50,000-volt, American Transformer Co., oil-cooled transformer, and a rotary rectifying switch, designed jointly by the Research Corporation and the Raritan Copper Works. Shortly after starting the commercial treater, on account of experiences at some other plants, air choke-coils were placed in circuit with the high-tension terminals of the transformer to protect the windings from puncture caused by excessive voltages due to surges.

At that time the plate treater was considered the most practical for our work, and designs were made along these lines. It was decided to use cast-iron as far as possible in the construction, but the question of the most suitable material to use for discharge wires furnished a perplexing problem. The gases were extremely corrosive, and tests made on wires of iron, steel, nickel, monel metal, aluminum and various copper alloys, proved all to be unsatisfactory. Tungsten wire was tried and found to stand up very well, but, on account of its cost and stiffness it did not seem practical. The solution of the problem was the employment of lead strips, one inch (2.5 cm.) wide, sharpened on the edges and set transversely between each pair of collecting plates. These have been perfectly satisfactory, the original strips still being in use.

The treater, as constructed, consisted of a rectangular cast-iron chamber, 8 ft. (2.4 m.) wide x 6 ft. (1.8 m.) high x 16 ft. (4.8 m.) long, set over a lead-lined hopper connecting with a sludge tank through a launder. Collecting electrodes, consisting of 6-inch (15 cm.) lead strips, were hung parallel with the gas flow, through cast-iron bars which also carried the cover plates. The lower ends of the strips were guided by slotted iron bars resting on flanges cast on the lower edges of the frame end plates. Cast-iron I-beams, carried on each side of the treater on high tension pedestal insulators, formed the high tension bus bars, and these carried four cast-iron channels running trans-

versely through openings in the sides of the treater, which supported the discharge electrode frames. It was thought likely that considerable trouble would be experienced with discharge electrodes breaking, and, to provide for easy repairs, these electrodes were set in rectangular cast-iron frames provided with lugs on each side of the top, the whole thing being thereby supported on two of the transverse channels. A cover was placed over each of these electrode frames so that, by simply lifting off the cover, the frame beneath running half the length of the treater was easily accessible and could be lifted out bodily, if nccessary.

As to durability, cast iron has proved very satisfactory in the sides and top; however, wherever there has been an intense electrical discharge, as from the discharge electrode frames, the iron has been quickly corroded. Lead, however, has proved entirely satisfactory under all conditions, and all iron discharge frames and guide bars have been replaced by lead-covered wrought iron.

In our operation, the gases leaving the Doré furnaces pass first into a four-foot (1.2 m.) diameter, sheet-iron flue about 40 feet (12 m.) long, then into a brick flue 6 ft. (1.8 m.) wide by 7 ft. 6 in. (2.3 m.) by 80 ft. (24 m.) long. A centrifugal fan, operated by a 40-H. P. motor, is placed on the end of this flue. This draws the gases out and forces them through iron connecting flues tangentially into the base of a circular brick settling chamber, 16 ft. (4.8 m.) in diameter by 17 ft. (5.1 m.) high. The whirling motion imparted to the gases in this chamber assists materially in depositing the particles of dust. An iron flue, 3 feet (0.9 m.) in diameter, leads from the center of the top of this chamber into a horizontal brick flue, which, in turn, opens into the scrubbers, the treater being connected to the scrubber outlet.

It will thus be seen that enough settling is secured in this system to remove practically all the values that are present in the form of dust, before the treater is reached; the only material passing to the treater being true fume. The flue and scrubber system are the same as were in use before the treater was built, consequently, the values which have been recovered by the treater would have been lost under former conditions.

The average analysis of the dust deposited in the treater is as follows:

	Percent
Selenium	6.5
Tellurium	6.0
Arsenic	10.0
Antimony	28.0
Lead	9.0
Bismuth	2.0
Copper	0.9
Silver	800 oz. per ton
Gold	1 oz. per ton

The total recovery averages 29.2 percent of the silver and 6.6 percent of the gold caught in the whole flue dust system.

Of the total amount treated in the furnaces, this is 0.24 percent of the silver and 0.022 percent of the gold.

All elements are highly oxidized, and silver and gold are combined with the base metals present in extremely insoluble forms, all attempts to remove them by acid treatment having been unsuccessful. It is also interesting to note that the silver in treater sludge runs about twice as high as in scrubber sludge. Gold runs about the same.

The cost of operating has been very low. The volume of gas treated will average about 6,000 cubic feet (170 cub. m.) per minute. The power required is about 2.5 K.W., at a voltage of 35,000 to 40,000. As to labor, one man working one or two hours per day can keep the treater clean and in good running condition. Aside from the substitution of lead-covered frames for the cast-iron previously mentioned, very few repairs have been necessary.

It will be noted that the gases, having previously passed through a system of flues and a water scrubber, are comparatively cool and saturated with moisture. Attempts have been made, at times, to treat the dry gases coming fom the flues directly, cutting out the scrubber. The results obtained under these conditions are much poorer than when the scrubber is in circuit. The temperature is, of course, much higher, being about 300° F. (149° C.) in the former case to 150° F. (66° C.) in the latter. The deposit is extremely dry and light, so that particles falling off the electrodes are carried out by the moving gases. The corona

is not so good when dry gas is used, and if the voltage is raised there is much more sparking-over than when wet gas is passing.

In our case the presence of suspended moisture appears to be a very desirable condition to satisfactory precipitation of the fume. The injection of steam has been tried but did not give satisfactory results.

Recently, a system of sprays has been placed transversely in the lead flue leading to the treater inlet through which the gases are forced to pass, and with this arrangement we have secured better results than with any other, a number of tests having given silver escaping as low as two or three ounces (55 to 85 grams) per day. This, however, is while operating at less than the full furnace capacity.

The results obtained with the first installation have, on the whole, been so satisfactory that it was recently decided to build a second treater of sufficient capacity to give us practically complete precipitation of fume with additional furnaces operating.

For a number of reasons, among them being better insulation, more substantial construction, greater economy of space and ease of cleaning, it was decided to build the new treater of the tube type. From results obtained in numerous tests on pipes of varying dimensions, lead pipes, 18 inches (45 cm.) in diameter by 12 feet (3.6 m.) long, containing a single central discharge electrode, were found to be the most satisfactory.

The discharge electrodes, to be used in these pipes, are made of ⅞-inch (2.2 cm.) steel shafting covered by extrusion with a star-shaped layer of lead. These electrodes are supported firmly over the pipes, and as they are stiff they require no steadying inside the treater. This is a very desirable feature. Most of the discharge at the start takes place from the sharp ridges extending the length of the electrode. However, when they have become coated with a deposit of dust the discharge is very uniform over the whole surface. With these pipes and a voltage of from 85,000 to 90,000 it has been possible to get over 99 percent precipitation efficiency, at a gas velocity of 4.5 feet (1.35 m.) per second.

The electrical apparatus secured for the new treater consists of two 10-K.W., Fort Wayne, direct-connected, rotary converters,

so arranged that they can be used interchangeably as a motor-generator set or as rotary converters. As a rule, they will be operated as a motor-generator, in which case the generator is separately excited by the regular 220-volt lighting current. Alternating current at 25 cycles and up to 200 volts can be obtained from these machines.

The transformer was made by the American Transformer Co., and is of 10 K. V. A. capacity. It is oil-cooled and has five taps giving 50,000-62,500-75,000-87,500-100,000 volts at a primary voltage of 200. By means of these taps, together with rheostats in the generator field and in series with the low tension A. C., it is possible to secure extremely fine regulation of the high-tension voltage.

An arm-type rectifier of Research Corporation design is used, and has proved very satisfactory in all the tests which have been made.

With this complete installation we expect to be able to treat up to 12,000 cubic feet (340 cub. m.) per minute of silver furnace gases and to recover 99 percent of all the silver and gold which they contain.

DISCUSSION.

Secretary J. W. Richards (*Communicated*): This paper brings out very strikingly the commercial importance of a thorough understanding of what might otherwise appear almost an academic question, viz., the volatility of the metals, or, more accurately expressed, the complete vapor tension curves of the metals. The maximum vapor tension of mercury has been measured from 0° C. to 880° C., but for all other metals we have only a few scattered points on their respective curves or else no data at all.

In the case of silver, we know only approximately the temperature corresponding to 760 mm. vapor tension. This is 2,040° C., which is more than 1,000° above its melting point and a far higher temperature than prevails in the smelting or cupel-

ling furnaces from which silver fume is escaping. We need to know, therefore, its vapor tension curve at temperatures approximating 1,000° C., and it is possible to obtain a first approximation to this by studying the principle of corresponding vapor tensions, as is explained in the writer's Metallurgical Calculations, Part III. Using the vapor tension curve of mercury as a basis, the vapor tensions of silver at temperatures down to its melting point have been estimated, and may be found in the reference given.

Basing a calculation on these data, the engineers of the Raritan Copper Works estimated that they were losing annually $30,000 of silver as fume, and on the strength of this calculation installed the precipitation plant described in Mr. Aldrich's paper. It is interesting to know that the net result of the first twelve months' operation of the fume plant resulted in saving $30,000 worth of silver, or just the calculated amount.

Such satisfactory agreements of theory and practice lead us to the assurance that any problem concerned with the vapor tension of the metals can now be satisfactorily handled by engineering calculation. It is, in fact, possible to calculate the vapor tensions of the metals below their melting points, which gives us the data necessary for understanding such processes as the Sherardizing process of zinc-coating iron, and the calorizing process of depositing aluminium, which depend on the vapor tensions of zinc and aluminium respectively. We can even obtain a first approximation to the vapor tension of the metals down to ordinary temperatures—data which may have an intimate connection with the starting of an arc between cold metallic terminals. The vapor tension of zinc, for instance, at room temperature is approximately 1×10^{-15} mm. of mercury.

It follows from what has been very briefly explained, that vapor tension curves of the metals are of considerable importance and interest to the chemist and metallurgist, because they enable him to understand quantitatively the volatilization losses in smelting processes and to control other processes depending upon the vapor tension of metals, while they concern the electrical engineer directly in any exact study of the starting and the maintaining of an arc between metallic terminals.

President L. Addicks: This paper seems severely metallurgical, perhaps, for a meeting made up largely of electrical engineers. But this process of electrostatic precipitation, which started in the recovery of values from smelter fumes, has spread over a large field, such as the recovery of sulphuric acid from chemical works, getting rid of the dust nuisance in cement work, and the smoke nuisance of the ordinary boiler plant, and is now being extended to dealing with fog; but as Doctor Cottrell is here himself, I am going to ask him to please tell us a little about the general question, and particularly about the new work which he is now exploiting in regard to fog precipitation.

F. G. Cottrell: What I have to say today will be in large measure the continuation of a brief outline of work that I had the pleasure of presenting to the Midwinter Convention of the American Institute of Electrical Engineers last February in New York. At that time, we were trying to get together plans for an equipment at the Panama-Pacific International Exposition for carrying out some tests on the possibility of an extension of this same work to the problem of fog dissipation. Necessarily, that goes back to the very beginning of the problem. It was Sir Oliver Lodge's interest in the problem of dispelling the London fogs that first drew attention of the general public to this whole problem of electrostatic precipitation, and it was in his laboratories in England that experiments along that line were conducted, as well as in the precipitation of smelter fumes. When the work was first taken up in this country, a decade ago, it was felt that it would be practically impossible to get much effective public interest in the fog situation until practical results in industrial applications had been obtained. The smelter-fume litigation was just then at such a critical stage throughout the country that it served as a particularly good problem to begin with, as it was absolutely imperative that something be done and the smelter interests consequently were willing to take a relatively long chance and spend money freely even on a new process that must have seemed to many of them at least rather visionary.

Now that this phase of the work has been pretty successfully developed, it seems time to take the next step and to see what can be done toward dispelling fog in the open atmosphere.

Again, this new problem may very likely have to be divided into two rather distinct lines of attack, the one aimed at dispersing fog from fixed spaces of relatively quiescent air, such as railroad yards and crossings, narrow channels and eventually, perhaps, congested city districts where it may be possible to erect a permanent overhead electrode system and allow the electric field and current thus produced to act for some seconds or even minutes on the same mass of foggy air. These conditions of an essentially quiescent atmosphere seem to be those with which Sir Oliver Lodge worked in his experiments on fog.

The other line of attack would be directed toward the more nearly instantaneous treatment of air in rapid motion, with respect to the electrode system, as would be the case when the fog is accompanied by wind, or when operated from a moving vessel. In this latter case it would probably be necessary to apply much more intense and local electric fields to the air, the equipment approximating more nearly to the electrode systems now used in the treatment of industrial gases, but of very much lighter construction. It would also be necessary, at least in the case of a moving vessel, to devise some method of supporting and carrying out these electrode systems in advance of the vessel, as by a tethered helicopter or other air craft, whose power could, of course, be supplied through its tether line.

Aside from all these accessory mechanical details, which must eventually be worked out for the complete practical solution of the problems presented, there is also a considerable amount of pioneer investigation to be done on the electric technical side.

The Panama-Pacific International Exposition at San Francisco seemed to present particularly good possibilities for attempting the solution of some at least of such problems, especially as regarded the equipment which would be available, so an effort was made to get co-operation between the different engineering interests, manufacturing companies, the American Institute of Electrical Engineers, the Bureau of Standards, the Exposition authorities, and the people who would naturally be interested in the fog problem, such as the steamship companies, railroads, and others. This has resulted in having quite a unique equipment of apparatus at disposal, with which to carry on these experiments, largely under the direct supervision of represen-

tatives from Stanford University and the University of California, and technical men here on the Coast, as well as visitors from further away.

Mr. C. H. Thordarson, of Chicago, has taken the lead in designing and providing equipment. He has had the courage to undertake to place on the grounds at the Exposition, first, a 350,000-volt transformer of 100-kilowatt capacity, in the Palace of Machinery, with which we are just commencing experiments, and following that, in a separate building, put up by the Exposition Company for the purpose, a standard frequency (60-cycle) transformer of a rated capacity of 1,000 kilowatts and 1,000,000 volts. The latter apparatus, unfortunately for your present visit, is not completely assembled, as yet, but those of you who go out to the grounds tomorrow, will, I think, have the opportunity of inspecting it. The building in which it is housed stands just east of the Palace of Machinery, and looks like an enlarged railroad shed, such as is used for a single locomotive, both ends being open, except for canvas curtains, to permit of bringing out the high tension lines. The transformer is being rapidly assembled there, and a large metal-lined concrete vat has been provided for the purpose, with this housing over it.

The entire transformer weighs approximately 15 tons, about half of which is made up of the magnetic circuit. It represents some interesting new features of transformer construction, aside from its capacity. The secondary is composed of some 90 miles of aluminum ribbon, with some 270 miles of paper ribbon insulation.

The experimental work now going on upon the ground was started this past year, chiefly at the University of California, in the way of testing out the electrical conditions surrounding the operation of high tension transformers and rectifiers and developing, possibly, new types of rectifiers, which would be better suited to these extreme voltages than those already available. The rectification of the current for the work we have done at the smelters has been chiefly by mechanical means, *i. e.,* simple commutation of a larger or smaller portion of the alternating current wave. This is very convenient up to potentials of say 250,000 volts, but when one goes to anything above that, peripheral velocities of the rotating parts become extremely difficult to

handle, due to the large diameter necessary to get insulation, and it was a question whether some other form of rectification might not be preferable, even though it might have other shortcomings.

You will see in the work in Mr. Thordarson's space in the Palace of Machinery, where the 350,000-volt transformer is now in operation, some interesting applications of rectifier principles, by the use of air blasts on the spark itself.

The General Electric Company has kindly furnished one of its oscillographs, so that we can follow the actual phenomena of wave forms more closely than has usually been possible in the field. It is proposed to carry the rectified current out of the building onto the roof, and there experiment with its action on the fog.

Funds for various smaller special equipment, included in both last year's work at the University of California and that now under way at the Exposition, have been furnished by the Smithsonian Institution, and the Research Corporation is at present paying the salaries of three men who are giving their whole time to these experiments at the Exposition.

The original plans for this work, like nearly everything in connection with the Exposition, were entirely upset by the outbreak of the European war, and at one time it looked as if the whole project would have to be abandoned, but it was finally decided to go ahead as best we could in any case. This and other circumstances beyond our control have delayed the actual work upon the ground, until now the closing of the Exposition looms close ahead, and the most favorable season for fog observation is already past, so that at best it will probably be possible to make only a bare beginning before the close of the Exposition. It is still hoped, however, that some data of at least a suggestive nature may be gathered here which will point the way to more extended and systematic investigations at points selected with special reference to their suitability for fog observation, for the Exposition grounds are not ideally located for this purpose. There is, to be sure, often plenty of fog in the vicinity, but for the most part it is high, very thin, and accompanied by strong and gusty wind, which makes qualitative observation very difficult, especially for the early stages of the experimental development.

The problem of clearing fog differs from that of treating smoke and fumes in flues in several important respects; for instance, in the latter case it is manifestly necessary actually to deposit the suspended matter on the electrodes to accomplish the effect sought, while in the case of fog, if even a considerable coalescence of the minute particles into large ones could be effected, it would become much more transparent, even aside from the more rapid settling of the drops. On the other hand, some new difficulties are to be expected, such as the matter of insulation, because the whole apparatus is of necessity continuously immersed in the wet atmosphere.

What is now needed is to get some actual first hand experience in direct handling of these conditions, in order to secure a concrete and intelligent conception of the problem as such.

The advantageous conditions at the Exposition for assembling a wide range of special equipment and securing the interest and constructive criticism and suggestions of resident and visiting engineers and specialists of all kinds, has made it seem that the opportunity should be taken advantage of to the full.

Something would probably have been done before this, making use of the equipment at some of the smelting works, had it not happened that the more powerful installations have all been at points where there was no possibility of getting fog conditions to carry out any experiments. It now practically amounts to taking up Lodge's old problem, which he attacked with the simple apparatus at his command, such as the electrostatic machine and to some extent afterwards with vacuum rectifiers, and trying to reduce that to the more distinctively modern type of engineering practice.

I have taken the time today to bring only this to your attention because of the opportunity that you have, while here, at least to see the apparatus which we are working with. If it were not for that, I would not attempt to make any report on this matter until the work was quite a little further forward. It was hoped the equipment would be here earlier than it proved possible to get it on the grounds, and that we might perhaps have working, by this time, some actual demonstrations on a small scale, at least, of the precipitation of fog, but that has not been possible. On the other hand, you will, perhaps, have the chance to see the

apparatus more in detail in its separate parts before it is completely assembled, and this may be in some respects of more interest to you, as electrical engineers.

I might also say in this connection that any of you who are interested in seeing the actual operation of one of the standard precipitating units, such as is used for smoke and fumes in industrial plants, will find one furnished by the Western Precipitation Company in operation at the Co-operative Metallurgical Exhibit on the space of the Bureau of Mines in the Palace of Mines, at the Exposition. You will also there find a detailed model of one of the large commercial plants, and a collection of samples of various materials which are at present being precipitated at different works by this type of apparatus—all the way from cement dust and smelter fumes to desiccated milk and eggs.

Chairman Addicks: I feel quite sure, after Doctor Cottrell's record of brilliant success in the smelter field, it will not be long before our friends in London, instead of groping through the dark, will be dodging million-volt discharges from the lamp posts, as a substitute. The paper is open for discussion, and I know Doctor Cottrell will be glad to answer any questions.

John H. Finney: Is it absolutely necessary to go to such high voltages as 350,000 to 1,000,000 volts, to get results in fog dissipation? That is rather high voltage from an operating standpoint.

F. G. Cottrell: I am glad you asked that question. I do not want to lay any stress on the fact that we needed a million-volt transformer to carry out this work. It was simply that we were going to have it here at the Exposition, and it might be a long time before we had another occasion or opportunity to try out such work, and so we are going to make the most of the opportunity. I think we can work with relatively small potential on the fog work, if we put our electrodes close enough together. That is the situation we met during the smelter work. The first experiment conducted, and the experiments on which the original installations were based, were with potentials of 5,000 to 7,000 volts, and the first permanent installation was on the basis of 17,000 volts. Since then the technique has been gradually worked up to 250,000 volts, on fair-sized installations,

handling perhaps 20,000 cubic feet of gas per minute, but the practice is apparently settling down today to voltages of from 30,000 to 100,000, as being the most convenient, under present conditions. The higher the voltage, the wider apart the electrodes can be set. For example, using a pipe, or system of pipes, with the discharge electrodes in the axes of the pipes, the higher the voltage available the larger the diameter of the pipe that can be used, and consequently, the smaller the number of construction units in the apparatus, with less trouble from accretions, from spacing of wires and work of that kind. On the other hand, the length of pipes must be increased, in order to get a proper proportion between the diameter and length, and a point is soon reached where you again encounter an awkward form of construction, and where the advantages in a smaller number of individual pipes are overbalanced by installation difficulties and other problems of that kind. So, viewed from these general criteria, the work seems to have become pretty well standardized, say, between 30,000 and 100,000 volts in the majority of installations.

In the case of the fog work it seems probable that a great deal of it will be done in-between these voltages, but in order to be safe, and not overlook possibilities while we are at it, we were glad to have the opportunity to carry it up to higher voltages.

It is also, of course, quite possible that in the case of suspending electrodes freely in the air, it may become more desirable to get wider spacing, in order not to have to use too rigid a system, mechanically, to hold the electrodes in place for uniform distribution. But the fact that we had an opportunity of getting this apparatus together seemed to be a good time to carry the whole program through, and we are making a pretty vigorous effort to do that. I wish here to emphasize again that the idea of assembling this apparatus at the Exposition is not merely for the fog work. That is simply one incidental extension of the work in which I happen personally to be particularly interested. It is there for general electrical experimentation concerning high voltage, including transmission work and other phenomena of interest to the electrical engineer. Professor H. J. Ryan, of Stanford University, has very kindly taken an active interest

in that work, and we are looking to him and others to make very good use of the equipment in such other directions.

PRESIDENT L. ADDICKS: About the amperage, as there are such tremendous voltage factors, does not extending it a ship length ahead require tremendous power?

F. G. COTTRELL: Not necessarily, at least judging from what we have learned from the treatment of industrial gases. For example, take the work at Riverside. They are treating there about a million cubic feet of gas a minute, and using only about 30 to 40 kilowatts, which includes auxiliary apparatus, such as shakers, rectifier motors, etc., as well. If you figure what a million cubic feet of gas a minute is, as compared with the pathway of a ship, you can see that the two are at least of somewhat the same order of magnitude. In other words, the sort of work we have to do in the atmosphere, in order to get practical results, is fairly comparable with that already accomplished in the flues of commercial plants. The hot gases of the cement kilns cited above will probably consume less energy, for technical reasons that I need not enter into in detail at the moment, than an equivalent amount of damp, foggy air would, but at the same time the problems are conceivably of at least the same order of magnitude, and we have no reason, *a priori,* to expect the new one to be prohibitive.

W. D. PEASLEE: I have had occasion to do some research work in connection with stimulation of plant growth by electrical means, and it was necessary during the performance of the work to secure very high direct voltages. I have been investigating and would call to your attention a method of rectifying, which, to my mind, is quite superior to the rotary or any other form of rectifier—that is, the "kenetron tube" recently developed by Doctor Langmuir in the research laboratory of the General Electric Company. In this tube we have a rectifier operating at considerably above 95 percent efficiency, which will give direct current voltage of pretty nearly anything we want. I think Doctor Langmuir said he did not recognize any limit to the voltages they could secure, depending almost entirely on what voltage our alternating current transformers give us. It gives a good connecting link between the alternating and direct current systems,

will maintain high pressure, and is as simple a link as the transformer. It removes the rotating part of the rectifier or other apparatus of that kind. I want to bring it up at the present time as being possibly of interest to those who desire to introduce a machine of this kind.

C. H. Aldrich (*Communicated*): Dr. Richards brings out a point of great importance, particularly to those engaged in the refining of the precious metals, *viz.*, the value, from practical considerations, of more complete determinations of their vapor tension curves. I fear, however, that he gives us credit for

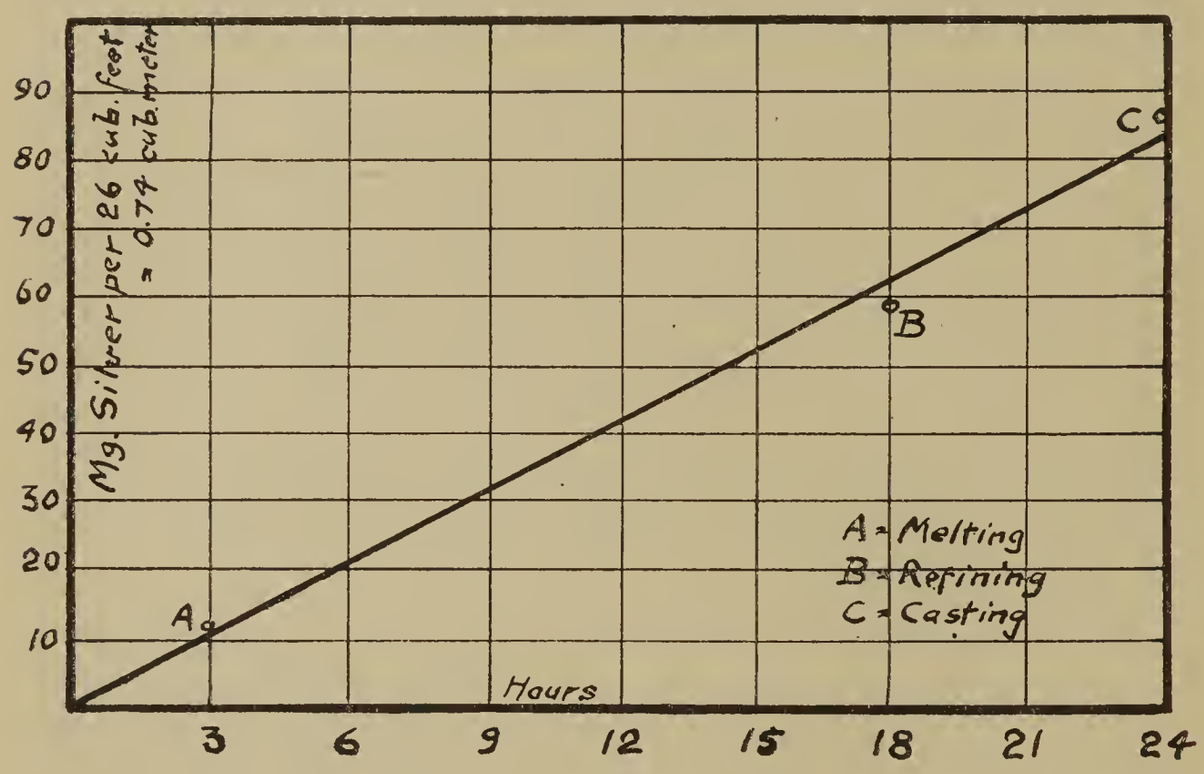


Fig. 1.

better work along this line than we are entitled to. While calculations were made based on vapor tension, so many interfering elements entered in that they could not be regarded as conclusive, and many filtration tests were made before we finally felt assured that we knew very closely the values that were escaping. It is true, however, that our actual recoveries during the first year of operation of the treater checked very closely with our estimates, although we would hesitate to claim the degree of accuracy mentioned by Dr. Richards.

Anyone who has observed carefully the operation of melting

pure silver has seen abundant evidence that it has a very appreciable volatility. In making our tests we have been able to secure data that indicates that the volatility increases with the increase in purity of the metal. This is shown strikingly on the preceding curve, based on samples of furnace gases taken throughout the refining of a charge of electrolytic slimes.

The kenetron tube, mentioned by Dr. W. D. Peaslee, has been tested out on our treater, under actual working conditions, and has given very good results. Tests covering long periods of time have not been made, however, so that the life of the tube and cost of renewals are still elements of doubt.

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ELECTROMETALLURGICAL INDUSTRIES AS POSSIBLE CONSUMERS OF ELECTRIC POWER.

By Dorsey A. Lyon and Robert M. Keeney.

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I. INTRODUCTION.

Utilization of hydro-electric power in electrometallurgical industries, aside from purely mechanical purposes, may be of two kinds. The electric energy may be used to supply the heat necessary for the performance of the chemical reactions of a metallurgical process, or the electrolytic action of a direct current may be employed for extraction of metals, either in a reduction process or a refining process. In discussing this subjcet it is well to distinguish between established industries which are producing metals and alloys at a profit by use of the electric current, and the many processes which are either still in the experimental stage or have not even passed the paper stage of development of a patent. That is, we consider electrometallurgical industries as commercial operations which are now consuming large blocks of electric energy, while processes which are not in commercial operation are only prospective consumers.

Disregarding electrolytic refining processes, the applications of electric energy to metallurgy, when considered from a commercial viewpoint, may be classified as follows:

Industrial Stage.	Experimental Stage.
Manufacture of aluminum.	Electric furnace smelting of copper ore.
Electric furnace manufacture of ferro-alloys.	Electric furnace smelting of zinc ore.
Manufacture of pig iron in the electric furnace.	
Manufacture of steel in the electric furnace.	

In this discussion only the above industries and experimental processes will be considered as possible consumers of hydroelectric power in large quantities. Electrolytic refining processes are not classified above, as they are either so closely interwoven into a cycle of metallurgical operations as one single step as to prohibit their operation as a separate industry, or the electrolytic process is such a small scale operation as to be unimportant as a large consumer of power. An example of the former is the electrolytic refining of copper. As at present operated, the electrolytic copper refinery, while it may not be located at the copper smelter, is usually owned by a smelting company upon which it largely depends for its supply of unrefined anode copper. It has also been found advantageous to locate copper refineries near the market for refined copper, which is New York. An extreme illustration of a small-scale electrolytic operation which is not worth considering as a large consumer of power is electrolytic refining of gold and silver. All of the above electrometallurgical industries are adaptable to self-contained development in a single plant, under proper conditions. Practically none of these industries consume less than 1,000 h.p. in a single installation. There are many electrometallurgical processes in successful use for the extraction or refining of metals which do not consume large amounts of power because the yearly yield is small, as in the case of gold and silver, or production is reduced by the small market, for example, calcium, magnesium or bismuth. If there was a demand for them, the two former metals might be produced profitably in conjunction with the manufacture of sodium, which, while a larger consumer of power than either calcium or magnesium, is not a large consumer in comparison with other electrometallurgical industries.

There are many electrometallurgical processes which might be considered as possible consumers of power, but in the majority of

cases, they exist only as patent specifications and have not yet been tested by either small or large experimental work. As an immediate market for power, most of these processes are of no interest to the power producer.

The commercial success of an electric furnace or electrolytic industry, in which the basic process employed is technically sound, may depend largely upon the following factors:

(1) The market for the product.

(2) The cost of electric power.

(3) Freight rates.

(4) Labor conditions.

(5) Cost of raw materials.

Of these factors, all of them except the cost of electric power will influence the success of any manufacturing project to a considerable degree.

Market for the product is of equal importance to the cost of power, for if there is not a steady market for the product, permitting a profit on the investment, a low cost of power will not necessarily result in the ultimate success of the enterprise. There is only a limited market for electrometallurgical products, so that while a good profit might be made on paper by comparing the cost of production with the average selling price, the enterprise would be a failure with a large part of its products unsold. Where market competition is strong, success, as in any line of business, would depend to a large extent upon the efficiency of operation, quality of the product, and the ability to sell the product at as low a price as any manufacturer.

Among many persons the idea prevails that the success of an electrometallurgical enterprise depends almost entirely upon a low cost of electric power; but, as a matter of fact, a strong market demand for the product is of equal importance to the low power rate. In general it is true that reduction processes require a very low power cost, especially operations producing a large tonnage of a comparatively cheap product, which compete with combustion processes, as for example, electric smelting of iron ore and zinc ore. On the other hand, electric furnace refining processes do not require an extremely low power cost to attain

commercial success, as many electric steel furnaces are operated at a profit on a power cost of 1 cent per kilowatt hour, or $65.70 per h. p. year. Few electric furnace reduction processes can operate successfully with a power cost of over 0.30 cent per kilowatt hour, or $20 per h. p. year, and to be measurably assured of commercial success requires a power cost not over $10 to $15 per h. p. year. We wish again to emphasize the statement that the commercial success of an electrometallurgical enterprise does not depend entirely upon the cost of power.

Freight rates have a large influence on the success of such a project, and in general it may be stated that in the Western part of the United States no electrometallurgical enterprise producing a tonnage product would stand much chance of success unless it was located within a few hundred miles of the seacoast, because of the high freight rates prevailing in the West as compared with Eastern rates. The short distance to water shipment has been a large factor in the success of Norwegian and Swedish electrometallurgical plants, as well as of the work in Switzerland and the French Alps. Practically all of their product is exported to foreign countries by water, while most of their ore and coal or coke is shipped to them by sea. With the exception of an electrometallurgical plant located to utilize some specific raw material near by, the cost of raw materials will depend largely upon freight rates, for in the majority of cases, at least, the ores used must be brought from a distance.

II. PRESENT COMMERCIAL STATUS OF ELECTROMETALLURGY.

In order to get an idea of the extent to which electric power is utilized in electrometallurgical processes it may perhaps be well at this time to review briefly the present commercial status of electrometallurgy.

ALUMINUM.

All aluminum manufactured today is produced by an electrometallurgical process, either by the Heroult process or the Hall process, both of which are essentially the same. In the United States the Hall process is used and in Europe the Heroult process.

The production of aluminum in the United States has increased materially since 1912, but exact figures are difficult to obtain (owing to statistics being given for recent years as consumption). The consumption in 1913 amounted to 72,379,090 pounds, of which 23,000,000 pounds was imported during the calendar year. The actual production in 1913 in the United States has been estimated at 65,000,000 pounds, and today probably 150,000 h. p. is in use for this purpose.

Until recently the production of aluminum in the United States was entirely controlled by the Aluminum Co. of America, owners of the Hall patents, which have now expired.

On the expiration of these Hall patents in the United States, a company was formed by French financiers interested in L'Aluminium Francaise, under the name of the Southern Aluminum Company. A plant is in course of construction at Whitney, N. C., on the Yadkin River, where a total development in high water of 100,000 h. p. is possible, although the average power will be about 45,000 h. p. The capacity of the plant to be erected will be 20,000,000 pounds of aluminum per annum. This Company continued its construction work up to the outbreak of the European war, when it became embarrassed by the then existing financial condition and so was obliged to discontinue its work. Such being the case, the Aluminum Company of America is the only real producer. Some second quality metal is put on the market by concerns which simply remelt scrap and junk.

TABLE I.

World's Production of Aluminum.

(Metric Tons)

(From Statistical Report of the Metallgesellschaft, Frankfurt am Main)

	1911	1912	1913
United States	18,000	19,500	22,500
Canada (exports)	2,300	8,300	5,900
Germany, Austria-Hungary, Switzerland	8,000	12,000	12,000
France	10,000	13,000	18,000
England	5,000	7,500	7,500
Italy	800	800	800
Norway	900	1,500	1,500
Totals	45,000	62,600	68,200

In Europe the aluminum industry has progressed as rapidly as in the United States. From the table given on the preceding page, it will be seen that Europe in 1913 produced about three times as much aluminum as the United States, but this country leads in individual production with France second.

FERRO-ALLOYS.

The growth of the ferro-alloy industry in Europe has been rapid since 1899, but comparatively slow in the United States. There are about 25 plants engaged in the manufacture of ferro-alloys by the electric furnace method, as compared with two plants making alloys in the electric furnace in the United States. There is, however, an electric furnace ferro-silicon plant in Canada, at Welland, Ontario.

There are several reasons why the growth of this industry has been slower in America than in Europe. Hydro-electric power is not as cheap here and not so favorably located for the receipt of raw material and the sale of product. The water-power sites can not be developed so cheaply as many of the foreign sites, where the cost of electric power per horsepower year varies from $7 to $15 as compared with $15 to $30 in the United States. This refers to power delivered at the manufacturing plant transformers. In Canada power is somewhat cheaper, but is often located in inaccessible places. Most of the Norwegian and Swedish plants are located on tidewater, or navigable rivers. French works are within a couple of hundred miles of Marsailles. The use of ferro-alloys in the manufacture of high class steels did not advance as rapidly in the United States as in Europe, and owing to less favorable natural advantages, electrochemical and electrometallurgical industries in general have not had so rapid a progress and growth.

A large proportion of the ferro-alloys used in the United States is imported, as, although there is a duty, local manufacturers do not supply the whole demand. This is true of about one-half of the ferromanganese and one-half of the ferrosilicon used in the United States as well as a large part of the ferro-tungsten. More ferrotitanium and ferrovanadium are manufac-

tured here than abroad. The ferrochromium production just about supplies the local demand.

Imports of ferro-alloys into the United States during the year ending June 30, 1913, were as given in the table below. The rates of duty were those in force previous to the passage of the present tariff, under which all duties were reduced considerably, in most cases being made 15 percent *ad valorem*. Hence it may reasonably be expected that imports will increase at some time in the future.

TABLE II.

	Rate of Duty	Quantity (Tons)	Value	Value per Ton
Ferromanganese	$2.50 per ton	128,136.55	$5,484,829	$42.80
Ferrosilicon, over 15 percent silicon	20 percent	9,257.18	574,494	62.06
Chromium and Ferrochromium.				
Value $200 per ton or less	25 "	459.09	53,624	116.80
Value more than $200 per ton	20 "	68.29	35,667	563.55
Ferrophosphorus. Value $200 per ton or less	25 "	81.38	3,689	45.33
Molybdenum and Ferromolybdenum. Value more than $200 per ton	20 "	7.00	15,939	3187.80
Titanium and Ferrotitanium,				
Value $200 per ton or less	25 "	19.21	9,213	479.59
Value more than $200 per ton	20 "			
Tungsten and Ferrotungsten. Value more than $200	20 "	634.30	795,467	1215.75

PIG IRON.

The electric furnace for smelting iron ore is of advantage only in localities where charcoal and coke are expensive and electric power cheap. The electric furnace consumes one-third of the carbon used by the blast furnace in the manufacture of pig iron, and hence its use may be advantageous where coking coal is scarce, and charcoal expensive. In considering the electric smelting of iron ores with regard to its commercial status at the present time, it must be remembered that the electric furnace is in this case competing directly with the blast furnace product regardless of its location, due to the cheapness of water haulage. It is not like the aluminum or ferro-alloy industry, where the electric furnace has the field to itself, because of its technical and commercial superiority over any combustion process. Hence in

proportion to the amount of pig iron produced we can not expect to show nearly as large a rate of increase for the electric furnace process as in the case of aluminum and ferro-alloys.

Although the electric furnace has been successful in the smelting of iron ores in other countries and in those districts in this country which are favorable to the same, we have only one electric furnace pig-iron plant of two furnaces with a total capacity of about 7,000 horse power. This plant is located at Heroult, California. Although the electric furnace uses only one-third of the coke or charcoal that the blast furnace uses, all solid reducing agents are so scarce and expensive on the Pacific Coast of the United States as to increase greatly the cost of electric smelting and practically to prohibit the blast furnace smelting of iron ores. Attempts have been made to use oil, but they have not yet proved successful.

While advances in electric smelting of iron ore have been satisfactory, considering that its field of use is limited, the actual tonnage capacity of electric pig-iron furnaces is small. This is quite clear when it is remembered that the total erected capacity in power consumption of electric iron smelting furnaces, 47,000 horse power, would produce about the same amount of pig iron per day as one modern blast furnace of 450 tons output per 24 hours.

STEEL.

As in other electrothermic processes, development has not been so rapid in the United States as in Europe. There were only 14 furnaces in this country, in 1913. The average capacity per charge of the furnaces already built is 3.7 tons, whereas that of the furnaces under construction is 4.5 tons, an increase of 21.6 percent. The total charge capacity of these 14 furnaces is about 250 tons per charge, and the total charge capacity of the furnaces under construction will be 170 tons per charge.

In the first years of its development, the electric furnace process was considered as a competitor of the crucible process only, for making high-class steel from scrap iron and scrap steel; but with the successful operation of larger furnaces the electric process is likely to become an important adjunct to the Bessemer and open-hearth processes as a means of super-refining the molten

products that they yield. The electric process, however, does not appear to be destined to supersede either of these methods, as greater efficiency and economy are obtained by a combination of any two of the three processes as a duplex process. The success of recent experiments has obtained for the electric process a definite place as a super-refining method. In time, preliminary refining will probably be done mainly in the Bessemer converter, the process being finished in the electric furnace, or the open hearth. In Europe, the electric furnace process for making steel of the highest grades is rapidly superseding the old crucible method, because of its greater economy of operation and the possibility of using minerals of lower grade.

COPPER.

So far as we are aware, no copper ores are being treated at the present time in the electric furnace in this country.

However, more or less experimental work has been done upon the subject, and, as a result of this work and reasoning by analogy, there seems no good reason why, under favorable circumstances, copper-bearing ores cannot be as successfully treated in an electric furnace as in a combustion furnace.

ZINC.

Although, as previously stated, more progress has been made to date in the electric smelting of zinc ores than with the electric smelting of any of the non-ferrous metals except aluminum, and metals forming ferro-alloys, such as those of silicon, chromium and tungsten, the process is nevertheless still largely in the experimental stage. There is no plant operating on a commercial scale in this country. One small commercial plant is in course of erection at Keokuk, Iowa, by the Johnson Electric Smelting Company. It appears that the experiments conducted at Hartford, Conn., for several years have proven successful enough to warrant the installation of a small commercial unit to test the process further. The Johnson process and the process used at Trollhättan, Sweden, are essentially the same. However, Johnson claims to have overcome the difficulty of condensing zinc vapor into zinc, instead of into blue powder, which has been the great problem at Trollhättan.

III. THE POSSIBILITY OF DEVELOPING ELECTRO-METALLURGICAL INDUSTRIES IN THE WESTERN PART OF THE UNITED STATES.

Having thus briefly stated the present status of the electro-metallurgical industry, we can now consider what the chances would be for the development of such an industry in the inter-mountain and Pacific Coast region of the United States.

ALUMINUM.

Raw Materials and Labor.

The ores and other raw materials necessary to the manufacture of aluminum are bauxite, cryolite, coal and caustic. Such being the case, all the raw materials necessary, with the exception of coal, would, at the present time at least, have to be brought in from some other point, if an attempt were made to manufacture aluminum in any of the inter-mountain and Pacific Coast States; and in California it would be necessary to ship in coal from some other point as well.

Bauxite is mined in the United States in Alabama, Arkansas, Georgia and Tennessee. Arkansas is the leading producer. An aluminum plant located at any point in the Western part of the United States would be obliged to depend for its source of bauxite upon some of these Eastern States, as no bauxite is known to exist in the Western United States in large quantities. It has been proposed by some that alunite might become a source of aluminum, but all processes for the extraction of alumina from silicates are still very much in the experimental stage. About 10 percent of the bauxite consumed in the United States is imported from Europe. The Southern Aluminum Company, with its plant in North Carolina, proposed to import all of its bauxite from France during the first few years of operation.

The average price of bauxite at the mines for 1913 was $4.75 per long ton. A typical bauxite analysis is as follows:

	Percent
Insoluble	12.13
Loss on Ignition	28.97
Alumina (Al_2O_3)	57.56
Iron Oxide Fe_2O_3	1.34

About four long tons of bauxite are necessary per ton of aluminum, which will cost at the mine in Arkansas or Georgia.

$19. This bauxite, if used in the Western part of the United States, must be hauled from the East by rail, or by rail and water. It is doubtful if raw bauxite could be laid down at any point in the West for less than $14. Therefore, the total cost of bauxite per ton of aluminum produced from it would be $56. Four tons of bauxite would produce two tons of alumina. The cost of purification would bring the cost of alumina to $38 per ton of 2,000 pounds. Two tons of alumina produce one ton of aluminum so that the cost per ton of aluminum with bauxite at $14 would be $76.

Some freight charges could be saved by purification of bauxite to alumina at the mine or nearby. The cost of alumina at the mine would be about $19.50 per short ton, or about $28-$30 in the West. The alumina for one ton of aluminum would thus cost $55-$60, a saving of about $9 per ton of alumina, or $18 per ton of aluminum made from it.

In the manufacture of aluminum, 0.1 ton of cryolite, sodium-aluminum fluoride ($AlF_3.3NaF$), is consumed by volatilization of the electrolyte per ton of aluminum made. Cryolite is produced only in Iceland. Some aluminum manufacturers substitute an artificial fluoride for the cryolite, using also some calcium fluoride (fluorspar). Cryolite is worth about $24 per long ton in New York, or 1.1 cents per pound. Shipped to the Western part of the United States, cryolite would cost about $35 per long ton or 1.5 cents per pound.

In the electrolysis of alumina in the electric furnace about 0.7 pound of carbon anode is consumed per pound of aluminum produced. In France and Germany these electrodes are manufactured at the larger aluminum plants from coke at the cost of 2.5 cents per pound. The cost of manufacturing them in the West, with coke costing at a minimum of $10 per ton, or charcoal at $8 per ton, would be about 5 cents per pound. Electrodes could be brought from the East or Europe at a cost of 5 to 6 cents per pound, f. o. b. San Francisco.

The cost of other materials such as caustic soda and of fluorspar will not be discussed here, as the amount used is small, and their cost has been included in other estimates.

Labor costs in the West for manufacture of aluminum will be higher than in the Eastern States or Europe. In Europe $1 per

day is an average wage for laborers at aluminum plants, while it is $1.50 in the Eastern United States and $2.50 in the West, outside of mining camps.

Power.

The manufacture of aluminum requires direct current, so that the use of high-tension alternating currents, as delivered by Western companies, would mean the transformation of this high current down to a lower voltage for use in a motor generator set. Allowing for transformer, motor generator, and line losses, this would result in the delivery to the furnace from the direct-current generator, of about 85 percent of the energy delivered to the transformers. If we assume that the plant would be operated on a flat rate of only $10 per horse power year for a 11,000 volt alternating current, the cost of power at the electrolytic furnace, on the basis of 100 percent load factor, would be $11.76. While it is sometimes stated that an industry like the manufacture of aluminum can be operated on a 100 percent load factor, this can not be used as a safe figure in calculating costs. The manufacture of aluminum, however, will maintain a higher load factor than some other similar industries, as for instance electric furnace manufacture of iron and steel, because of the small units employed, and the ease of replacing a broken-down unit with a new one without much additional capital outlay caused by keeping reserve units. The largest aluminum furnaces do not require over 150 h. p. each, while electric iron and steel furnaces have a capacity of from 300 to 12,000 h. p. Another point influencing the load factor maintained is the market for the product manufactured. This is especially true of a new company which has to build up its market. When buying power on a flat rate instead of by the kilowatt hour, with a variation of load factor, say between 85 and 100 percent, any curtailment of production due to market conditions will result in a heavy charge to the electrometallurgical company for power which they are not using. For this reason a load factor of 90 per cent is assumed in calculating the cost of power. This would increase the cost of direct current at the aluminum furnace to $13.06 per h. p. year, or 0.2 cent per kilowatt hour.

Cost of Production.

The following estimate of cost of production of aluminum is based upon a plant requiring 25,000 horse power or more, in units of 100 to 150 horse power.

Cost of Production of Aluminum Per Ton (2,000 pounds) with Conditions as Above Stated.

2 tons of alumina, @ $28.75 per ton	$56.50
200 lb. of cryolite, @ 1.5 cents per lb.	3.00
1400 lb. electrodes, @ 5 cents per lb.	70.00
Other fluxes, etc.	10.00
28,000 kilowatt hours, @ 0.2 cents per kilowatt hour	56.00
Labor	70.00
Repairs	10.00
Amortization, depreciation, 5 percent each	18.00
Interest (6 percent)	10.00
General expenses	20.00
Total	$323.50 per ton, or 16.22 cents per lb.

Allowing $15 per ton for freight to New York and $20 per ton for marketing expense, the total cost per ton f. o. b. New York would be $359.50 per ton, or 17.98 cents per pound; in round numbers, 18 cents per pound.

Market.

The average price for No. 1 ingot metal at New York during 1913, generally for spot metal rather than future deliveries, was 23.6 cents per pound, but in 1914, 18.6 cents per pound.

Hence it is evident that in order to avoid a shut down in dull times, a company manufacturing aluminum in the Western part of the United States must be able to sell aluminum in the New York market at 18 cents per pound or less.

Aluminum manufactured in the West, would at present have to compete with a domestic production of 65,000,000 pounds of aluminum, and imports of about 30,000,000 pounds. It is stated that the domestic production of aluminum will in the future be increased by at least 20,000,000 pounds per annum due to the Southern Aluminum Company starting its plant, so that inside of two years all of the present imports except 10,000,000 pounds will be supplied by domestic producers. It is also stated that the Aluminum Company of America contemplate doubling their present capacity at a plant in Tennessee; if this be done it will

eventually add a possible production of 40,000,000 pounds per annum, or a total future output of 30,000,000 pounds more than the present market demands. Thus it is clear that any company, starting business now, will have strong competition to meet in several years, which would be from the very start of its operation, as its plant could not be completed for several years. This competition would exist in spite of the fact that the consumption of aluminum in the United States has increased at the average rate of about 7,000,000 pounds per annum for the last five years. While at this rate of increase of consumption, contemplated increased output would no more than supply the domestic demand, it is not probable that the consumption will maintain quite as high a rate of increase. Foreign manufacturers will also be much more active in the New York market in the future owing to the decreased tariff.

Conclusions.

Taking into consideration the above statements, we are of the opinion that the manufacture of aluminum in the Western part of the United States would not prove profitable to a manufacturing company.

Even if electric power could be had at $10 per h. p. year, the high freight charges on raw materials and product, and increased labor costs over Eastern wages are such as to raise the cost of production so high that in periods of depressed market the cost of aluminum made in the West would about equal the lowest selling price. In this connection it is also well to consider the fact that invariably manufacturing costs increase in times of business depression, due to decreased output. Also as such a plant would buy power on a flat rate basis, any decrease in output would result in a great increase of unit cost, due to the continued charge for power regardless of its being used.

A study of the preceding data shows that freight rates on raw materials, supplies, and product would contribute largely to the cost of the production of aluminum in the West. While India bauxite might be shipped to the West very cheaply, little is known about these deposits, and their development is in the distant future. An example of the high cost of materials due to freight is seen in electrodes. They can be purchased in the East

at 3 cents per pound. On the basis of 0.7 pound consumption of electrode per pound of aluminum, electrodes at 5 cents per pound increase the cost of aluminum by 1.4 cents per pound.

As previously stated, labor costs would also be considerably higher in the West, and technical men, such as chemists and engineers, also receive a higher rate of pay.

All of these factors would contribute to the cost of production. At the low price of aluminum in 1913, a company manufacturing aluminum in the West, would have about broken even if it sold all its product. At a price of 20 cents per pound a profit of 2 cents per pound could have been made. A production of 10,000,000 pounds per annum would require a plant costing about $4,000,000. This production would give a profit of $200,000 per annum, or 5 percent on the actual investment. This is generally considered much too low a margin of profit for safe investment, due to unforeseen conditions which might arise and increase the cost. Estimates previous to operation are usually found low in practice. It is probable that the Eastern producer could sell at a profit at 18 cents per pound, for it has been estimated that the cost of production of aluminum at Niagara Falls is not over 15 cents per pound.

A company now a producer of aluminum with a market for its product, and an intimate knowledge of the industry would possibly manufacture aluminum at a small profit in the West, especially with cheap power, but we see no reason why such a company should come to the West at the present time. Apparently, an established company owning its bauxite supply and having a market, is the only sort of a concern which would be able to operate a plant in the West without losing money, and they could not make as much profit there as in an Eastern plant.

PIG IRON.

Raw Materials and Labor.

The raw materials necessary for the manufacture of pig iron in the electric furnace are iron ore, either hematite or magnetite, limestone, and charcoal or coke. There is no choice as to the kind of iron ore, as the electric furnace will handle either hematite or magnetite. Charcoal is preferable to coke in electric furnace manufacturing of pig iron because the energy consumption

is less, due to the possibility of use of the shaft type of furnace with charcoal, and operation of the furnace is more steady. Coke can be used, however, in the rectangular type of furnace without a high shaft.

Iron ore deposits of good grade are more or less plentiful throughout the Western States, but unfortunately the cost of transporting it to a point where it could be utilized might prohibit its use. Moreover, it is estimated that Chinese iron ore containing 60 percent iron can now be laid down at the Pacific Coast ports at a cost of about $5 per ton. Such being the case, we will assume that the cost of iron ore would be $5.

Limestone deposits are also more or less abundant throughout the West, and so the cost of the same for use as a flux in the production of pig iron would probably not cause concern.

As before stated, charcoal or coke could be used as a reducing material. As the starting of a plant, charcoal would be the preferable material, but if the plant assumed great proportions, say using over 100 tons of charcoal per day, we believe that it would be necessary to use coke, on account of possible scarcity of charcoal. For the purpose of this paper, we will assume the cost of the reducing agent as being not less than $10 per long ton. About one-third of a ton of reducing agent would be necessary per ton of pig iron produced, costing $3.33.

Labor requirements are the same as in blast furnace manufacture of pig iron, and a minimum wage of $2.50 per day of eight hours is assumed.

Power.

Power will be considered as costing at the furnaces $11.70 per horse power year or 0.18 cent per kilowatt hour, allowing for transformer losses in reducing the voltage to 40 to 110 volts.

Cost of Production.

The following estimate is based upon an annual production of 50,000 tons of pig iron. The plant would consist of five electric furnaces of 3,500 horse power each, the whole plant requiring 18,000 horse power, including 500 horse power for various uses outside of the furnaces.

Estimated Cost per Long Ton of Producing Pig Iron in the Electric Furnace With Conditions as Above Stated.

1.6 tons of iron ore at $5.00 per long ton	$8.00
0.33 long tons of charcoal or coke at $10.00	3.33
0.25 long tons of limestone at $1.75	0.44
10 lb. of carbon electrodes at 5 cents	0.50
2400 kilowatt hours at 0.18 cents	4.32
Labor	5.00
Maintenance and repairs	0.50
Amortization, depreciation, at 5 percent each	1.70
Interest at 6 percent	1.02
General	1.40
Total	$26.21

Based upon the above estimate, the cost of producing pig iron by use of the electric furnace would be about $26 per long ton.

Market.

The market for the pig iron manufactured in any of the inter-mountain or Pacific Coast States would largely be a local one. At the present time, this market would probably not be very great, due to the fact that so long as pig iron sells from $20 to $25 per ton, there is little incentive to use it in foundry work, when scrap iron can be purchased at a much lower price. There is no large steel plant on the coast which would be a consumer of pig iron.

Another important factor lies in the cheapness with which pig iron from England, China and India can be laid down upon the Pacific Coast. Pig iron from any of these countries could be delivered at Pacific Coast ports for from $18 to $20 per ton. With the Panama Canal open, it is now possible to lay Eastern pig iron down on the Pacific Coast for about $18 per long ton, so that the foreign or Eastern producer could considerably under-sell the Western manufacturer.

Conclusions.

Although local conditions are in general favorable in some instances to the production of electric furnace pig iron, we may say that the enterprise does not appear to be feasible commercially in any of the Pacific Coast States, because of the high cost of raw materials, and market conditions. Nor would it be feasible commercially, to attempt to produce pig iron for conversion into steel, because Eastern billet steel can be brought to the

Pacific Coast at a total cost of $30.50 per long ton, which would probably be much less than it would cost to produce it in the localities above mentioned.

The high cost of production is largely caused by the high cost of iron ore, which is about double that paid by Eastern blast furnaces which are producing pig iron for about $10 per ton; and also by the high labor cost, which is about 70 percent more expensive than Eastern labor. The cost of reducing material is also high as compared with the cost of Eastern coke at the furnaces, in spite of the fact that the electric furnace uses one-third of the amount of coke used by the blast furnace. It would therefore seem that the cost of production alone would prohibit the success of an electric furnace pig iron industry in most of the Western States.

To assure commercial success, the plant should be able to sell its product in the Coast market, at as low a figure as $18 per ton. Eastern or foreign pig iron can be laid down at that cost. It is also quite likely that the market for pig iron, with the price as high as $20 per ton, will not grow very rapidly, for as before stated, it is cheaper to use scrap iron to make castings.

STEEL.

There are two courses of procedure for steel manufacture in which the electric furnace has been used; cold scrap iron and steel of either inferior or high-grade quality is melted and refined in an electric furnace with the production of steel of the highest grade, and equal to the best crucible steel and molten steel; or the product of either the acid or basic converters, or of the acid or basic open hearth furnace, is super-refined, or made into alloy steel, in an electric furnace. The steels thus made may be cast into ingots, or various shapes. It has been proposed to use the electric furnace for the manufacture of steel from molten pig iron, but with pig iron at $20 per ton the cost of so doing would be prohibitive. Steel made from molten electric furnace pig iron would cost at least $34 and probably over $40, while that made out of Eastern pig iron, which would have to be melted, would cost at least $30 and probably $35, and so could not compete with Eastern steel, which can be sold in the West for about $30.

As the high cost of pig iron prohibits the establishment of a "tonnage" steel plant, we will consider only an electric furnace plant for the production of high-grade steel castings and shapes, and bar steel.

Raw Materials and Labor.

The principal raw material used in the electric furnace manufacture of steel is scrap steel. While some scrap iron could be used, most of the material melted should be steel or wrought iron. Iron turnings, which in the open hearth are not especially desirable on account of oxidation losses, are about the most adaptable material for use in the electric furnace. There is not the high oxidation loss in the electric furnace that there is in the open hearth. Any scrap material used in the electric furnace must be small in size because of difficulty in operating a furnace on large scrap iron, due to short circuits. A large part of the turnings produced in the various foundries and shops throughout the West goes to waste at present, and could be obtained cheaply.

Power.

In the electric furnace manufacture of steel, electric energy is used at about the same voltage as in the production of pig iron or ferro-alloys, but the electric steel furnace can not maintain as high a load factor as the electric iron smelting furnace or the ferro-alloy furnace. For example, if it be necessary to transform an 11,000 volt current down to 40 or 100 volts, a transformer and line loss of 5 percent will occur. This, on the basis of 100 percent load factor and with power at $10 per horse power year would make the power cost $10.52 at the furnace. Owing to the intermittent nature of the electric furnace process in steel manufacture, a load factor of over 80 percent could be maintained only with difficulty. The power cost would then be $13.15, or 0.20 cents per kilowatt hour. If a lower rate were made on such power, an electric steel furnace could use "off peak" power to advantage on account of the intermittent nature of the process.

Cost of Production.

The following estimated cost of production of electric furnace steel is based upon an annual production of 25,000 tons and the

utilization of 4,000 horse power. There are so many combinations of furnaces of different sizes with which a plant could be equipped that we will not attempt to specify them. The estimate is based upon steel cast into ingot form.

Cost of Production of Steel in the Electric Furnace in the Western United States.

1.1 tons of scrap, @ $15 per ton	$16.50
Slag materials	1.00
Ferro-alloys	1.00
800 kilowatt hours, @ 0.20 cents	1.60
Labor	2.50
Maintenance and repairs	2.40
20 lb. of electrodes, @ 5 cents	1.00
Amortization, depreciation, @ 5 percent each	1.50
Interest, @ 6 percent	0.90
General	1.00
Royalty	0.50
Total	$29.95

With conditions as above stated, the cost of production of ingot steel in the electric furnace would be about $30 per long ton, to which would have to be added the freight rates to whatever point the steel was to be shipped.

Market.

There is very little market for billet and ingot steel on the Pacific Coast, and at the present time a tonnage steel plant manufacturing ingots for rails and heavy steel, would, as previously stated, probably not be able to compete in the market with Eastern or foreign products. There is a considerable demand for small shapes on the Pacific Coast, and considerable steel is used in this manner. A plant in the West casting steel into such steel shapes would possibly be able to dispose of its product, but a large part of the steel shapes used in the West, belong to machinery manufactured in the East, and most of this steel comes from the Eastern States.

Conclusions.

Considering the conditions as above stated, it does not look as if the manufacture of "tonnage" electric furnace steel in the

West would be profitable, as steel in the form of ingots, billets, rails or structural shapes can be laid down so cheaply on the Pacific Coast from the Eastern States or foreign countries as to render impossible the profitable manufacture of this steel on the Pacific Coast at the present time. While a small electric furnace foundry, manufacturing special steel shapes and using 500 to 1,000 horse power might be successful, it would not amount to much as a large-scale steel producer. "Tonnage steel" can not be made at a profit on the Pacific Coast at the present time. Also owing to the high cost of producing pig iron, it would be impossible to operate successfully a self-contained iron and steel plant, using either electric furnaces or combustion furnaces.

COPPER.

As previously stated, the electric smelting of copper ores is entirely in the experimental stage. Before it can be practiced commercially, much money and time must be spent on experimental work. While we believe it to be feasible under favorable conditions, the process has not yet reached a stage of development that would warrant it being considered as having been fully worked out. When some of the Alaskan deposits have been more developed, electric copper smelting may prove profitable at points along the Alaskan coasts, as the ore in this case could be hauled largely by water. As the process itself is not fully developed, we do not consider it worth while to give an estimate of the cost of smelting copper ores by electricity.

ZINC.

While the electric smelting of zinc ores is more advanced than the electric smelting of copper ores, it has not yet proved to be a commercial success, or in fact a technical success. Such being the case, it cannot, at present, be seriously considered as a source of consumption of power. However, the process of electric zinc smelting will doubtless be more fully developed in the near future, and it is quite likely that the electric smelting of zinc ores will consume considerable power. But at present, as in the case of copper, we do not consider the process sufficiently developed to warrant giving cost data.

IV. GENERAL CONCLUSIONS.

1. The market for hydro-electric power for electrometallurgical industries in general is not great, and under the best of conditions the part consumed in electrometallurgical industries will be small. We are nevertheless of the opinion that such industries will, in time, be established, but perhaps along different lines than at present, that is, than for production of aluminum, ferro-alloys, pig iron, steel, etc. It is doubtless true that the electric furnace will in time be quite generally used for the local production of steel castings, but an extensive use of the electric furnace for this purpose will not bring about any great consumption of electric power.

Therefore, if our analysis of the situation be correct, is it reasonable to expect that hydro-electric power companies may ultimately be able to dispose of a great portion of their surplus power by reason of the development of new electrometallurgical industries? We believe they will and for this reason:

At the present time, the metallurgy of the non-ferrous metals is being rapidly changed. The processes which were suited to the treatment of non-ferrous ores five or ten years ago are at the present time not able to meet the requirements, owing to the fact that the non-ferrous metallurgical plants of the country are called upon to treat ores which are of a lower grade than formerly, and are more complex. Such being the case, processes must be devised which will meet these requirements. However, we do not for a moment imagine that electro-thermic or electrolytic processes will prove to be the solution of the many problems which are at the present time confronting the non-ferrous metallurgist. Although such processes may greatly assist in solving these problems, we are of the opinion that research work, yet to be inaugurated and successfully carried out, will aid the metallurgist in devising processes which will meet his requirements. We believe that this will be true, especially as regards hydro-metallurgical processes, as treatment of the low-grade and complex ores above mentioned requires the use of cheap reagents, if they are to be treated at a profit. Such being the case, the hydro-metallurgical treatment of such ores may bring about the establishment of an electrochemical industry for the production of the

necessary reagents, and thus indirectly the metallurgical industry may bring about an extended use of hydro-electrical power. Whether this will prove to be the case or not, remains to be seen. It can only be determined by a careful investigation of the subject and extensive research work, which shall have for its object the finding of new uses for electricity in metallurgical work.

DISCUSSION.

President L. Addicks: I think papers of this character, while general in nature, are of particular value and interest, because when we figure on competing with the East in electro-metallurgical industries, on account of the cheap power on the Pacific Coast, we have to take two or three things into account. In the first place, power very rarely amounts to more than twenty percent of the total cost of operation, even though it be electro-metallurgical, while I think it is the common opinion among those that are not familiar with those particular industries, that it amounts to more than fifty or sixty percent. Take copper refining; we may say that it is fifteen percent of the total cost. In the second place, around New York City, with 100 percent load factor and a reasonably large load, say ten thousand kilowatts, we can generate from a certain class of coal a kilowatt hour for about three-tenths of a cent. I might say, however, that three-tenths of a cent does not include overhead charges, interest on the investment and so on. The third factor we have to consider out here is that any product to be salable must command a retail market. It would be useless to produce wire-bars here on the Pacific Coast because there is no place to roll them. If we were going to establish a copper refinery, that part of its output which goes into wire-bars would have to be taken care of by building a rolling mill alongside of it to turn them into wire and finally make a product that is salable. I do not think, however, that Dr. Lyon was justified in excluding copper refining from his industries. There are perhaps fifty million pounds of copper a month refined in this country on a custom basis.

I think the smelter companies would be very glad to build refineries here did conditions justify it. The recent extensions of the Great Falls Refinery and of the Tacoma Refinery in the last few months give evidence of that.

C. H. Booth: I agree in a general way with the features of Dr. Lyon's paper. I have read it with very great interest. It seems to me the real reason for the lack of development of electro-metallurgical processes on the Pacific Coast is largely due to the lack of a market. I am not claiming to have a great knowledge of conditions out here, excepting what I have personally observed in the last few weeks, but my general conclusions are that in the one field of electric steel melting and refining, regardless of the low cost of melting, the lack of a proper market will always be a severe handicap to any operation of that kind on the Pacific Coast. Even with cheap power and low cost materials, the limited tonnage called for is a distinct disadvantage. If the steel made here must go East to find a market, the cost of freight rates and the fact that power can be produced almost as cheap in the East, will more than offset any other advantage; so that my general thought is, being especially interested in the line of steel metallurgy, that the chief drawback to the manufacture of a heavy tonnage of steel on the coast is the lack of a market.

Apparently the authors of this paper are not entirely familiar with some of the recent developments in the electric steel melting field. Electric furnaces are today being built which produce steel cheaper than the fuel melting furnaces for the same tonnage. These facts have been well worked out and carefully checked for a period of two years. Such furnaces are today producing steel at $18 a ton with current at three-quarters of a cent per kilowatt hour, and materials at $11 per ton. The upkeep cost is low and the efficiency of the furnace is so high that it has been practical to obtain low cost operations, and to use electric power and still compete with fuel melting. With this one point of difference—the cost of melting with the electric steel furnace—I thoroughly agree with Dr. Lyon's conclusions. I would call your attention especially to page 158, where there is given a schedule of the operating cost of an electric steel fur-

nace. With current at the price given, steel could be produced for about $18 a ton. So that there is at least a difference of $12 a ton from Dr. Lyon's figures.

It makes no difference how cheaply you can make the steel out here, if you have no market for it it is hardly possible to do much with the product. Even if steel is substituted for iron, with the increased tonnage that might be obtained, still I can see no hope for developing a large industry here in the immediate future.

J. W. BECKMAN: The attitude that both Mr. Lyon and Mr. Booth take in regard to possibilities on the Pacific Coast, I take pleasure in disagreeing with. I think it is undoubtedly true if you only look to the near future that they are in the main correct in stating that there are small markets only, but this is a new country, and we are practically in the same position here as the East was before the Civil War. Before the Civil War the East would not do any manufacturing, since they thought they could not compete with England. As they could buy what they needed from England they saw no reason for manufacturing. The East has changed; it has been shipping for many years, and will ship for a long time to come, manufactured products to England. Here on the Pacific Coast everybody apparently is looking to the East, and the eastern part of the United States for their markets. I have often heard it said: "What is the use of manufacturing out here, they can beat us in the East." I think that is a wrong attitude for the people of the Pacific Coast to take. We are favored with enormous quantities of water power here, practically at tidewater. There are a number of powers right on tidewater, and a number just a few miles away from tidewater. We have, therefore, the same power facilities on the Pacific Coast to produce electrochemical materials that Sweden and Norway have, especially Norway, and the same opportunity for shipping these materials to the world's markets. My feeling is very strong that the Pacific Coast's future does not lie east from here, but it lies west and south from here. We have over half of the world's population facing the Pacific Coast. We should take care of that population's electrochemical needs, and we will do so provided we look at matters in the right way. If we look only to the East we are certainly going to let

everybody in the East, as well as Europe, take care of those markets that legitimately belong to us. Therefore, I feel that the broad-minded view is to look forward, not to what this generation can do, but build for generations to come, and start doing so now. That is a duty resting on the present generation of the Pacific Coast. There is an enormous future for this coast. I think a great part of the people on this western coast do not appreciate the opportunity this section of the country has. We have the Chinese and Japanése markets of unlimited possibilities. We have the northern part of Siberia, that we do not know so much about. There are also markets to be had in South America and Australia, and we might reach for markets even as far as India, and in years to come I believe my attitude will be proven correct. I think this attitude of belief in the possibilities of this coast and its future is psychologically the right one to hold. Mr. Lyon does not seem to have taken into consideration the fact that we can get aluminum oxide at a very low figure here, from a deposit in Utah that is being worked now, and great quantities of practically pure aluminum oxide is obtained from it. It is claimed that the product is obtained so pure that in many cases there is no need of any further refining. A reasonable freight rate has already been established by the Western Pacific Railroad for this aluminum oxide from those deposits to the Pacific Coast. This oxide is obtained as a by-product at a very low price, and it seems as though there is a big possibility for making metallic aluminum on the coast from this raw material.

Mr. Lyon says that all our electrodes are shipped here from the East. We have here on the coast one very large and permanent source for the manufacture of electrodes in what is generally known as lampblack. In the making of volatile products from oil there is always produced quite a quantity of exceedingly fine carbon with some heavy oil mixed in. In many cases this has been used as fuel under boilers, because of no other use for it. From my knowledge of electrodes I believe that there is a possibility of using this practically pure carbon in the making of electrodes, and using them in aluminum manufacture and in electric furnace work.

Pig iron manufacture is a very old process, and no radical

change has taken place in the manufacture until comparatively recently. Is it not possible that this extremely old process will be supplanted in time by an absolutely new process utilizing new agents? Take here on the Pacific Coast, for example, we have an abundant supply of natural gas and an abundance of fuel oil. We also have an abundance of cheap electric power. Couple this with the abundant cheap iron ore and it seems as if there must blossom forth an iron industry of large dimensions.

Along the coast there are great deposits of iron ore. About two hundred million tons are now located running sixty-four percent of iron. It is of interest to note that the United States Steel Corporation is running at the present time on fifty-six percent iron ore.

Why should we not look forward to the utilizing of new agents and methods in place of the old processes for the manufacture of pig iron?

Another point that has struck me in connection with Mr. Lyon's paper, and not referred to, is the question of treating refractory ores by electrolysis, in a fused electrolyte. I believe it might be possible by such a process to partly separate the different metals present in the ores.

President L. Addicks: I think Mr. Beckman as attorney for the defense has put the problem on its true basis. If we did not have cheap power here the whole matter would be impossible. Of course, in regard to aluminum we all of us have an aluminum mine in our back yards, but the difficulty has always been to get a deposit of adequate purity.

I will ask Mr. Seaver to tell us what has been done by the refractory companies in the direction of using alumina.

K. Seaver: Although I hardly feel qualified to speak with authority on all that has been done in this field by refractories manufacturers, I am glad to give any information in my possession. You are familiar with a brick made from the hydrous oxide of aluminum, one variety of which usually contains approximately fifty-six percent alumina in the brick, while another contains about seventy-seven percent of alumina. The characteristics of the two vary rather widely, but cover probably the extremes of alumina content available on any commercially exten-

sive scale. In general the fifty-six percent alumina brick is used to replace fire-clay brick, as it will naturally withstand higher heats. As to its action under varying chemical conditions, they are substantially such as would be inferred from the characteristics of alumina. They resist the action of clinker better than a fire-clay brick and are more infusible.

In reference to the brick running seventy-seven percent in alumina, it is being extensively tried out as a substitute for magnesia, or as it is more often termed "magnesite" brick in the open hearth and similar processes, thus far giving excellent results. In an extensive trial in the open-hearth furnace for the full run, it equalled that of magnesite. These results, however, should be taken at their true worth, and it is not yet safe in my opinion to say that it is a satisfactory substitute. Under normal conditions it can hardly be produced at the price at which magnesia brick are made.

In general, bearing in mind the length of time necessary to try any refractory thoroughly, I feel that a material of this kind must be tested out under every conceivable condition before a definite statement on the subject may be made. It shows great possibilities, however.

Secretary J. W. Richards: I wish to speak on several matters connected with the subject of this paper. The first is the possibility of producing aluminium on this coast. Mr. Lyon considers the cost of aluminium here and shipping it to New York. I believe that if such a plant were established here that the material would not be shipped East, but would be used to supply the local market and also the Japanese market, which is a considerable one at the present time. The principal raw material is bauxite, or its equivalent, and the question is whether it can be found west of the Rocky Mountains. If the by-product alumina from the Marysvale alunite deposits in Utah could be brought here at five dollars freight per ton, that might put a different aspect on the matter. Or, if bauxite were to be found on the Pacific Coast, there would be a possibility of establishing works here to supply the local market and the Japanese, or other foreign markets bordering on the Pacific Ocean.

In regard to the consumption of steel on this coast, in the paper

by Mr. C. C. Jones of Los Angeles, to be read this afternoon before the American Institute of Mining Engineers, it is stated that the consumption of steel on the Pacific Coast is nearly three million tons per year. That is not an insignificant market, although I received the impression from Mr. Lyon's paper that he thought the local market here was not worth considering. In fact, that is a respectable proportion of the total consumption of the United States. If there is such a market here, and if the statements made as to the cost of making steel in a properly designed electric furnace are to be relied upon, there is a distinct possibility of the Pacific Coast furnishing its own supply of steel castings and possibly manufactured shapes.

Mr. Lyon has omitted from his paper a proper consideration of the practical importance of the ferro-alloy industry, which has already begun operations on the Pacific Coast. Electric furnaces in Shasta County, California, which were producing pig-iron are now operating profitably on ferro-manganese, ferro-silicon, and ferro-chromium. There is a possibility, it seems to me, of firmly establishing those industries on this coast.

Mr. Beckman: I take exception to what Professor Richards has said about ferro-manganese. It is not possible to establish electric-furnace manufacture of ferro-manganese here with normal prices of ferro-manganese, war prices show a good profit. But establishing industries on artificial prices is bad policy.

Mr. Lyon: I would like to call attention to the fact that in this paper we have discussed the electro-metallurgical industries as possible consumers of electric power at the present time. Also that we state we believe electro-metallurgical industries will become large consumers of electric power, but that they will probably be new industries which will be developed in connection with metallurgical work, as for example, in the treatment of low grade and complex ores, etc. It is to be remembered that in this paper we are not discussing electrochemical industries, nor did we intend to intimate that we believe an electrochemical industry cannot be built up on this coast. On the other hand, we do believe that there are certain electrochemical and electro-metallurgical industries already developed in the East or foreign countries which could be profitably established on this coast. How-

ever, it is our opinion that the establishment of such industries at the present time would not consume all the surplus electric power which has been developed on the Pacific Coast or in the inter-mountain country. Our discussion of this subject has been from the standpoint of large consumption of electric power.

As to the idea of there being a large tonnage of steel used on this coast: Day before yesterday I was talking to one of the leading iron and steel metallurgists of this country on this subject and he stated that in his opinion it would be quite impractical for any one steel plant to attempt to turn out all the varieties of steel that are used on this coast, and that although there is a comparatively large tonnage of steel used here in the West, that this tonnage is made up of such a variety of shapes and sizes that the individual steel plant must of necessity be a small one. Then, too, steel can in general doubtless be produced more cheaply in the East than it can on the Pacific Coast at the present time. It is all right to say that a large tonnage of steel is used here in the West, and it may look on paper as if the establishment of a large steel plant out in this country would be a profitable venture, but I cannot help but disagree with those who believe this to be true, as I am quite sure there is no demand for the tonnage of steel that any large up-to-date plant would turn out.

Mr. Booth: Mr. Lyon assumes in the paper that the principal use of the electric furnace in steel making is to be as the refining agent in connection with the open hearth. There has been enough experience with electric furnaces to prove that there is a considerable saving in operation cost. To carry out the entire process in one furnace, of sufficient capacity and properly designed, will prove more economical and produce a better product with less labor, and there are also other features which will cut down the operating cost.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society in San Francisco, at a Joint Session with the American Institute of Electrical Engineers, September 17, 1915, President J. J. Carty (A. I. E. E.) in the Chair.

THE ELECTROCHEMICAL POSSIBILITIES OF THE PACIFIC COAST.

By J. W. Beckman.*

AVAILABLE POWER.

Potential Water Power on Pacific Coast.

Forty-three percent of the potential water power of the United States is to be found in the comparatively narrow strip of land bounded by the Rocky Mountains and the Sierras in the East, the Pacific Ocean on the West, by Canada in the North and Mexico in the South.

The U. S. Government gives the minimum potential water power in the whole of the United States as 26,736,000 H. P. Of this, 11,504,000 H. P. is available in the States of Washington, Oregon and California, divided up between them as follows:

	H. P.
Washington	4,932,000
Oregon	3,148,000
California	3,424,000

Developed Water Power on Pacific Coast.

According to figures compiled by Mr. W. E. Herring, of the Puget Sound Traction, Light & Power Company, it is evident that only a very small percent of the power available in these States, is developed. The following figures show the distribution of developed power:

	Developed H. P.	Percent of Possible Power
Washington	306,000	6
Oregon	105,000	3
California	430,000	8

Power in Alaska.

Alaska belongs to the West coast of United States. The potential water powers of Alaska have never been estimated, but

* Chemical Engineer, Great Western Power Company.

conditions in the Southeastern section of the territory especially are such that they promise in a way to rival Norway, as to cheap and abundant water power. So far only a very small fraction of the available powers has been developed.

COST OF ELECTRIC POWER.

The cost of electric power on the Pacific Coast has often erroneously been thought prohibitive for electrochemical industries.

Cheap Power.

Power can be obtained close to the generating stations as cheap, if not cheaper than, the prices generally quoted for power at Niagara Falls.

"Off-Peak" Power.

Of course, the power at the end of a long transmission line is considerably higher priced than close to the generating station, but even so, if the industries can operate on so-called "off-peak" power at such a point, big reductions are offered the consumer. The size of this reduction depends on the consumption, and may even amount to 40 percent of the prevailing price.

Great Western Power Company.

The Great Western Power Company, which operates the largest power house on the Pacific Coast, is able to furnish power, if sufficiently large blocks are desired, at such prices that even the fixation of atmospheric nitrogen carefully conducted would be a financial succeess.

The power house and power sites of this company, from which close to 600,000 horsepower can be developed in large blocks, are all located within easy reach of tidewater. As a comparison, attention is drawn to the fact that Niagara Falls is four times as distant from tidewater as the above mentioned power sites.

Besides proximity to tidewater, this power is favored by being surrounded with various raw materials essential to electrochemical and electrometallurgical operations. For these reasons this power is perhaps best fitted as a prime mover in the electrochemical development of the Pacific Coast.

If it is further realized that one-fifth of all the population of

the Pacific Coast resides around the San Francisco Bay, it is plain that this Company, which supplies this section with power, holds a key to the immediate electrochemical development of this part of the United States.

Speel River, Alaska.

There are, however, a number of other power projects which will be able to furnish power cheap enough to compete with the proverbially cheap power of Norway. Such power can be obtained in Alaska at the well-known project on Speel River, ideally located on tidewater.

The Dalles, Oregon.

Another project is that at The Dalles, Oregon, on the Columbia River, close to the newly-opened Celilo canal, which makes the whole of Columbia River navigable.

Undeveloped Power.

All through this section of the United States there is still a great deal of water power, the development of which is not yet even projected, and many of the sites are so located that their development would be exceedingly cheap; but on account of somewhat remote location, scarcity of population and lack of electrochemical enterprise, they might be failures if developed at the present time.

LABOR.

In a way it is a futile thing to formulate opinion as to labor and its conditions on the Pacific Coast while this terrific struggle is going on in Europe, where thousands of men, if not millions, are being permanently taken out of the labor market. But in spite of this, it is problematical whether the opening of the Panama Canal will have a marked influence on the labor market of the Pacific Coast.

Nationality of Labor.

It is significant of the labor on this Coast that it is composed practically exclusively of either native-born Americans, or of foreign-born Americans who have to a great extent lost touch with the European country from which they originally hailed.

Exceptions to this are naturally the Orientals and Hindus, who seem to devote the greater part of their activity to agricultural and logging occupations, and as is well known they are not met on the Pacific Coast, justly or unjustly, with a "Welcome." Through international "gentlemen's agreements," and through exclusion, the inflow of this type of labor has to a great extent been limited, if not eliminated.

The labor, therefore, that has to be counted with at present, is really the best type of European: The man who is familiar with both the language and the ways of the land, the man who is wide-awake among his own countrymen and has been able to shake the shackles of the congested foreign sections of the large Eastern cities, the squalor of its mining and manufacturing towns, and, escaping the padrone, has taken his destiny in his own hand.

It can, from this, be understood that industries operating on the Pacific Coast get the pick of the Eastern labor market.

Direct Importation of Labor.

For a long time much the same conditions will prevail. Since European laborers are gregarious, they go only to centers already established by their own countrymen, and from such a point they branch off.

Only when a large population of directly imported foreign European labor has collected in Pacific Coast centers, due to industrial advantages, will there be a direct influx of European labor of any magnitude to the Pacific Coast.

Cost of Labor.

The cost of labor does not differ very materially on the Pacific Coast from that prevailing in Chicago. An extensive investigation has been made of prevailing labor prices, and the following figures are the result:

Unskilled labor	$1.50 to $3.00 per day
Skilled labor	3.00 to 5.00 per day

The average working day is eight hours.

Labor and Climate.

The climate of the Pacific Coast should not be overlooked in considering labor conditions and labor costs. With the modern researches made into efficiency and the effect of climate on same, it is well to appreciate that the equitable climate of the Pacific Coast, with mild winters and cool summers, is very stimulating and the average annual output of a laborer is materially greater on the coast than in the East.

Trade Unions.

Labor is fairly strongly unionized in some sections of the Coastal States, while in others the open shop prevails.

RAW MATERIALS.

Refractories.

Magnesite: Considerable has been said recently about California magnesite, and too much cannot be said about it, since the California magnesite is extremely refractory, being practically pure magnesium carbonate. With suitable admixtures it should furnish an ideal material for furnace linings.

There are large deposits of this mineral in California, and so far these deposits have not been extensively worked.

Asbestos: Short as well as long fibred varieties are to be found in large quantities in California and other localities of the Pacific Coast.

Kieselguhr: Large deposits are found, of such nature that solid blocks can be cut out and used in furnaces and other constructions.

Fire Clay: Very high quality is being dug, and excellent fire brick are being produced on the Pacific Coast. The bricks have been giving better results in open-hearth operations here than the best standard fire bricks of the East.

Dolomite: Good and extensive deposits are found at various points on the Pacific Coast.

Quartz: Quantities of pure quartz deposits are available, in rock formation as well as sand.

Most of the materials mentioned above occur in various quite widely distributed points on the Pacific Coast, and mostly in easy reach of transportation.

Reducing Materials.

Anthracite: The Pacific Coast is not favored in the same manner as the East with high grade anthracite coals, at least not at present. Alaska is as yet only a potential producer of coal, but this territory promises to supply the West Coast in the near future with high grade anthracite coal, low in ash and sulphur.

Soft Coal: Alaska, British Columbia, and the State of Washington are all producers of soft coal, and at various places on the Coast lignites are located. These coals do not have any value at present, except for ordinary purposes.

China, Japan and Australia all supply the coast with coal, some of which is high-grade anthracite of quality and at prices which make it possible for them to compete advantageously with coal brought in from the East.

Charcoal: Many of the densely wooded districts of the Pacific Coast have great abundance of timber, which in many cases would really be improved if part of it were carefully cut, and burnt into charcoal.

Southeastern Alaska especially is covered by overgrown timber, ideal for charcoal burning. It is obtainable practically at no cost whatever, and the charcoal would provide a pure carbonaceous material, comparatively cheap, for reducing purposes.

Natural Gas: The enormous oil fields of the Southern part of California furnish in many cases, besides oil, great quantities of gas, an ideal reducing material in metallurgical processes.

Oil: Present in great abundance, much of it practically free from sulphur. It offers in itself all the essentials for reducing metals from their ores.

Present day technique has as yet not evolved ways and means by which the two latter reducing agents can be used with success in electrometallurgical processes, but since the essentials necessary in reducing exist in natural gas and oil, it is purely a question of application of thermal and mechanical details to make such processes operative.

Lampblack: As coke is obtained as a by-product in the manufacture of illuminating gas from soft coal, so a very fine lampblack is produced in gas plants operating with crude oil. The

lampblack formed is practically pure carbon, except for a small amount of heavy oil mixed in with it. A considerable quantity of this material is produced every day at the various gas houses along the coast, and forms an ideal reducing material, since it contains no ash and no sulphur. At present this material is a by-product, and offers in many cases the problem of how to most advantageously dispose of it.

On account of its physical condition and its purity it offers an ideal raw material for the manufacture of carbon electrodes, for which there already is a demand on the Coast, and this demand is bound to grow rapidly from now on.

Fluxing Materials.

Limestone: Large and conveniently located deposits of limestone of high degree of purity are to be found at many and varied locations on the Pacific Coast, offering ample, cheap and certain supply of this important mineral. With the cheap fuel available, burnt lime can be produced to advantage at about $3.00 per ton.

Salts: Especially in the arid regions of Southern part of California, in the deserts, there are large deposits of various salts. Sodium sulphate, sodium carbonate, sodium chloride, and sodium nitrate are all found. Sodium chloride is also obtainable very cheaply along the beaches of the Pacific Coast. The salt ocean water is evaporated in shallow basins by means of sun and wind, and deposits are formed of practically pure salt, suitable for industrial or domestic purposes. This salt can be produced and stacked ready for transportation for about $1.50 per ton.

What promises to be of interest not only to the electrochemical industries but also to the world at large is the occurrence of considerable quantities of potassium chloride in the Southern part of California. These deposits are being developed and will shortly be a source of potash to be considered for more than one purpose.

The increasing demand for boron and its compounds can be filled from the large borax deposits in the Pacific Coast States.

Metalliferous Raw Materials.

Iron Ores: That the Pacific Coast holds some unusual iron ore deposits, unusual both as to size and quality, is not always realized. The quality of some of the ore is such that it can compete with some of the best Swedish ores. There is no reason why the Pacific Coast, with abundant supply of high grade iron ores, quantities of cheap oil and charcoal, and hydro-electric power obtainable in great quantities at low prices, should not be an iron producing section of the world, the products of which would figure largely on the world's markets. The time is not distant when such will be the case.

All the necessities for an extensive steel industry are to be found in the shape of ores suitable for the manufacture of alloys such as ferro-manganese, ferro-chromium, ferro-vanadium, ferro-silicon, ferro-tungsten, ferro-molybdenum and others.

Barium, both in the shape of sulphate and as carbonate, is to be found in large deposits and in accessible localities.

Bauxite, suitable as raw material for aluminum manufacture, can be found; so also the tin ore *Cassiterite.*

Zinc occurs abundantly; in many mine operators' opinions, too abundantly in connection with copper ores, and the mining world is eagerly waiting for some commercial process to treat copper ores containing considerable amount of zinc, recovering both the copper and zinc.

Copper occurs in great quantities, and in lesser quantities *lead, silver, nickel, mercury* and *uranium. Gold* and *platinum,* occuring only in native condition, are of no special interest in this connection.

In making mention of these various metals, it is with the intention of showing the multitude of possibilities open to the electrochemist and electrometallurgist, and although many of these metals are at present obtained from ores found on the Pacific Coast, by means of operations more or less costly, there still remain possibilities where these methods can be substituted both economically and efficiently by utilizing new forces and new agents.

POSSIBLE INDUSTRIES.

From the foregoing it is apparent that there are a great number of industrial possibilities here, but there are a few that are perhaps more apparent than others.

Caustic Soda and Bleaching Powder.

The industry most promising at the present time, for an early development, is the manufacture of caustic soda and bleaching powder. This industry and its possibilities have been thoroughly investigated, and it is established that a medium-sized caustic soda plant could be operated not only successfully but very profitably on the Pacific Coast.

Potassium Chlorate.

Potassium Chlorate manufacture is another industry which should have special possibilities here, with the raw materials necessary for it produced on this Coast.

Calcium Carbide.

The demand for calcium carbide in South America is great, and also in the mining districts of the Western part of United States. The raw materials are obtainable here and the manufacture of carbide should become a flourishing industry on the Coast.

Nitrogen Fixation.

Nitrogen fixation industries seek very cheap power, and such power is available here, as well as a very large market for the product. The soil of the coastal region is getting quickly depleted of nitrogen, while in some sections the soil is physically well adapted for farming purposes but lacks nitrogen altogether. Artificial fertilizer is therefore a great and urgent need for this part of United States.

Iron and Steel.

This industry, as has been indicated before, has great possibilities on the Coast, and although the present electric shaft furnace plant in Northern California has not been a total success, there is every reason to believe that success would be won if past experience as well as present practice in Sweden were utilized,

together with the application of new principles using oil, or oil and charcoal, as reducing agents.

The demand for high-grade steel castings, produced by means of the electric furnace, is large here, and although there are now three small furnaces operating on the coast there is place for a number of others.

Cyanide.

The Pacific Coast should logically be the world's distributing center for cyanide used in gold extraction. With raw materials suitable for the manufacture of this salt available, electric power, and the market all close at hand, such an industry should flourish.

Aluminum, Lead, Zinc, Copper.

Aluminum manufacture, lead reduction, zinc production, and the electrolytic refining of copper are other electrochemical industries which should be developed on the Pacific Coast. Practically all of the blister copper produced here is shipped East for final refining, when in reality conditions are perhaps even more favorable for this process on the Pacific Coast, where the metal is produced, than in the East.

MARKETS.

Sweden and Norway are looked upon as the world's electrochemical countries *par excellence.* Cheap water power has been held up as one of the reasons of this position, and it is worth noting that if Sweden and Norway had as many opportunities for large, cheap power installations as there are on the Pacific Coast, these countries would dominate the world with their electrochemical products. But the electrochemical industries there would be total failures, even if the processes were working to a nicety, if they had no market for their products.

The total population of those two countries amounts to 10,000,000 people, which to a great extent have agriculture or fishing as their occupation, thus furnishing only limited domestic market possibilities. Still, the industries there are successes in spite of limited home markets, because they have looked to markets beyond the boundaries of their countries, entered the

world markets and there found outlets for their products. These markets are free and open to each progressive nation or individual.

Pacific Markets.

Electrochemical industries on this Coast have to be inspired with the same desire as those in Sweden and Norway, since the population of the Pacific is about 5,000,000 people. With more than half the world's population dwelling in lands facing the Pacific Coast, these markets are just waiting to be taken by industries located on this Coast.

It may justly be said that the greater part of these countries facing the Pacific Coast are populated by people that are still living under primitive conditions, and their demands are limited. Such assumption may be partly correct today, but earlier experiences show that as these countries get more and more in touch with the well organized nations of the world, their needs for the products of these nations increase correspondingly.

This fact is startlingly apparent from statistics obtainable from the Philippine Islands, showing the imports prior to American occupation of the Islands in 1899 and after.

Figures received from the War Department's Bureau of Insular Affairs show that imports have more than quadrupled during the fifteen years the Philippine Islands have been under U. S. control, while they were practically stationary during the six years prior to U. S. occupation. The increase is quite significant, indicating the growth of imports as a country gets in touch with more modern conditions.

Many of the South American and far Eastern markets are now open, leaving unprecedented commercial opportunities for industries located on the Pacific Coast.

FINANCIAL CONDITIONS.

There was a time in the history of the Pacific Coast when gold mines and oil wells were the only undertakings which would interest men with capital. Fortunes were made and lost over night. The Pacific Coast is outgrowing this neurotic condition.

Men with money are still eager to make more, but wild. sky-

high flights in the financial world have lost their interest; financiers are as conservative on the Pacific Coast as they are in New York City.

It is natural for the West to look East for capital, but it is also equally natural for the West to look inside of its own boundaries for capital. The time is not far distant when financially the Pacific Coast, although not emancipated from the East, since this is impossible, will walk side by side with New York and other Eastern money centers, equally prepared to take as well as to give assistance in the realm of finance.

CONCLUSIONS.

The Pacific Coast is still practically an untried country from the electrochemist's point of view. Enormous quantities of cheap, undeveloped power are still to be found, and developed power is available at prices such as rival the cheapest water power of the East. The natural resources of the Coastal districts are unlimited. They abound in minerals suitable for refractories and fluxing.

Charcoal, oil, natural gas, and lampblack from gas houses, as well as high grade anthracite, suitable for reducing purposes, are all obtainable on the Pacific Coast.

A great abundance of various kinds of salts and metalliferous ores are present in diverse localities of the Pacific Coast, offering unusual opportunities for electrochemical and electrometallurgical industries.

Conditions on the Pacific Coast are now ripe for various electrochemical and electrometallurgical undertakings. The manufacture of caustic soda is especially well adapted to this section; low salt cost, low fuel cost, cheap power and large market for the caustic as well as for the bleach assures immediate success to such an undertaking.

The labor obtainable is the very best, and is not higher in price than in Eastern centers.

The climate is ideal.

The financial conditions of the Pacific Coast are sound. "Blue-sky" laws protect the investor against wild-cat schemes.

Any industry operating on the Coast would have to look to

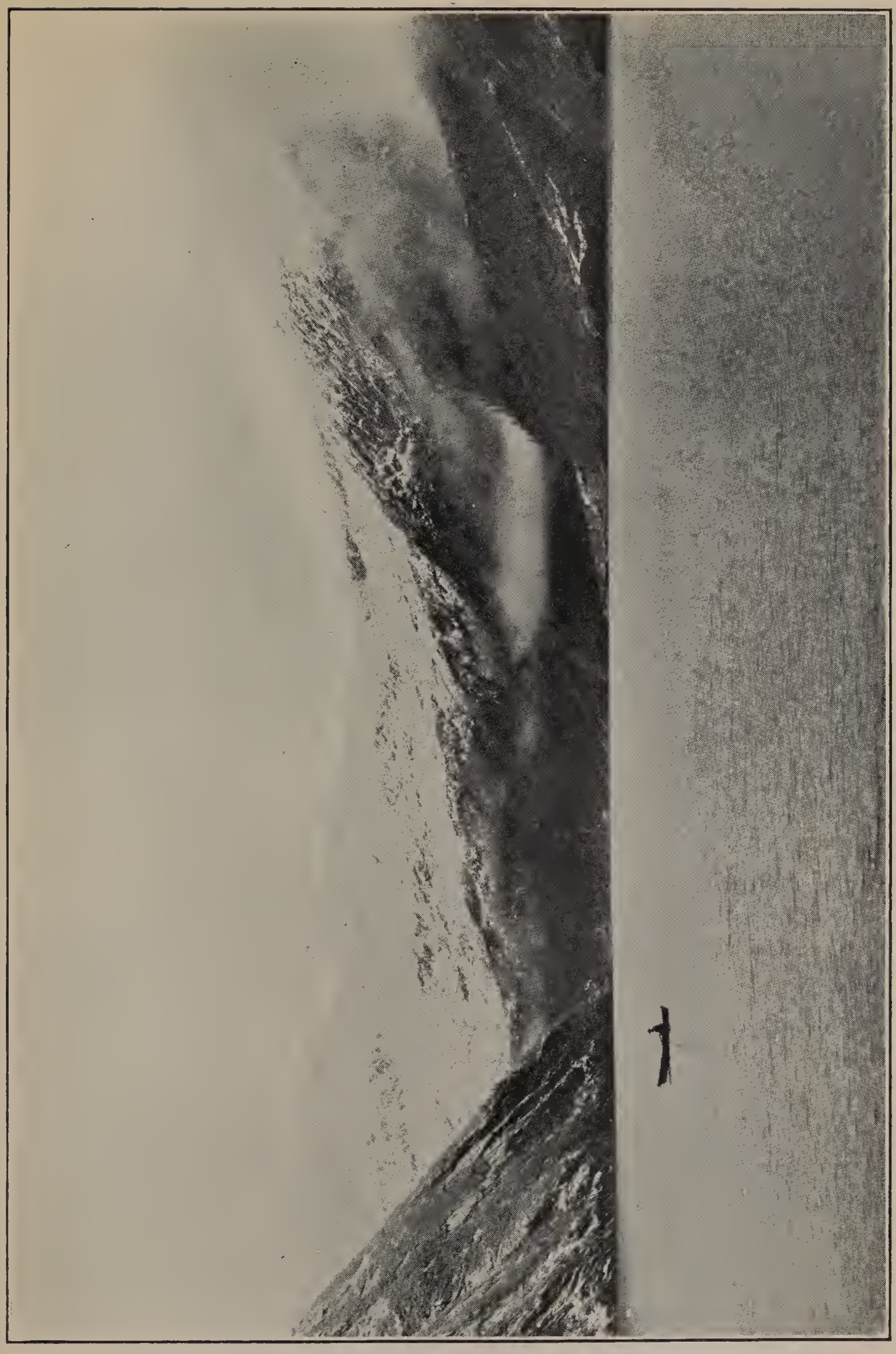
other markets than the local ones for its products. With more than half of the world's population facing the Pacific Coast, an industry here has greater commercial possibilities and opportunities than one located in Sweden or Norway, which have large nearby, fully developed markets, but also keen competition to contend with.

But for a few small electrochemical industries on the Coast, electrochemistry would be unknown here, excepting by its name. The Pacific Coast has as yet not financial strength, nor experiences enough, to build up these industries alone.

The possibilities are here; the Pacific Coast is quickly waking up to this fact, but is forced yet for sometime to look East for its electrochemical stimulus.

Will the East come West and give it?

[See Discussion page 191.]

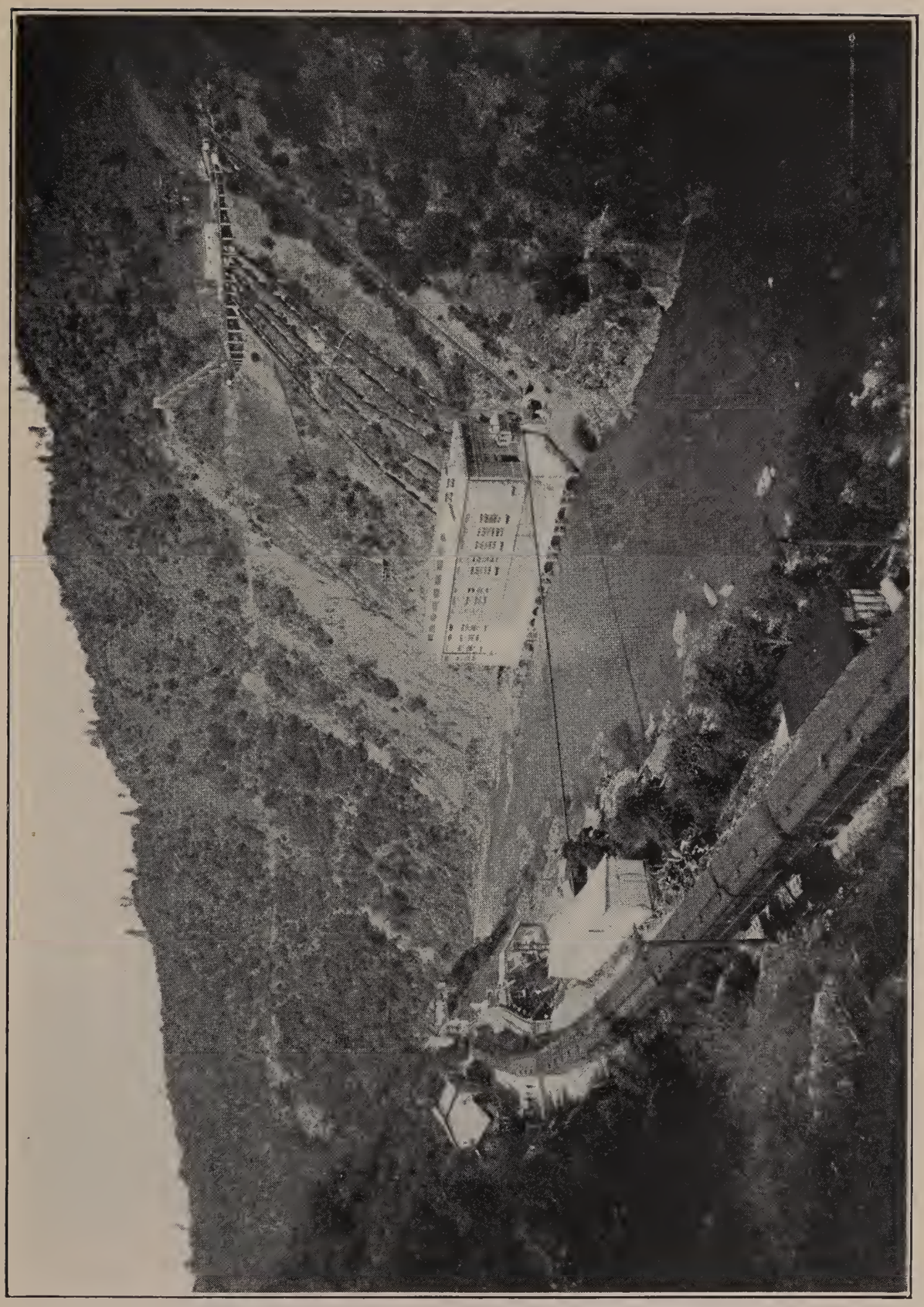


SPEEL RIVER POWER PROJECT, ALASKA.
Lake 727 ft. above sea, and 2 miles distant.

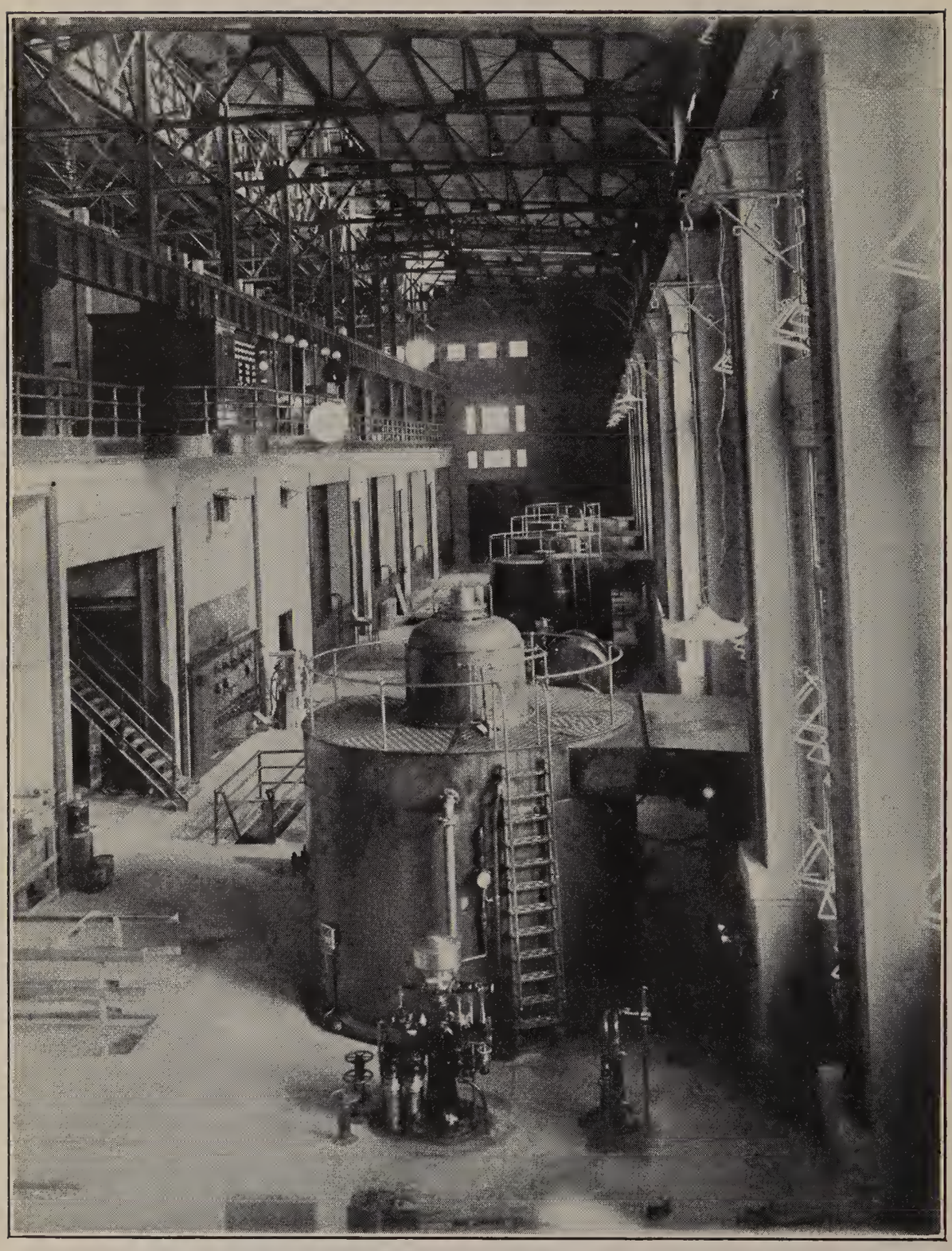
LONG LAKE POWER DEVELOPMENT.

COLUMBIA RIVER AT HEAD OF FIVE MILE RAPIDS.
(Extreme high water 90 ft. above low water at this point).

PRESENT AND PROPOSED WATER POWER DEVELOPMENT ON THE FEATHER RIVER.



BIG BEND POWER HOUSE.



INTERIOR OF BIG BEND POWER HOUSE.

KERN RIVER PLANT SOUTHERN CALIFORNIA EDISON CO.

DISCUSSION.

J. W. Beckman *(Remarks made in connection with presenting an abstract of his paper):* I can see no reason why we should not be able to show new developments in the manufacture of iron from iron ores, by means of utilizing new agents for it. We have here on the Pacific Coast not only iron ore, but we have a suitable fluxing material and we have the necessary reducing materials. We have hydrogen and carbon in the natural gases and the oils which are very abundant on the coast. Combine that with electric power, and it seems as if it would only be necessary to apply some mechanical process to it by which we could revolutionize the present methods of producing iron from ore.

The financial condition on the Pacific Coast is very interesting. The "gold rush" brought in many unscrupulous and reckless people, but as the gold rush has died down, and the people have had "to get down to brass tacks," it has changed altogether the financial outlook and the ways of handling money problems out here.

The market possibilities is the one great thing that really determines the success of an industry. If we on the Pacific Coast permit ourselves to do the same as they did in the East before the Civil War it will be a long time before we ever really accomplish what we are aiming to accomplish. In the East before the Civil War the general attitude was—"They can do it in England, they can do it cheaper in England, and what is the use of our doing it here?" They have changed that attitude in the East. The same apathetic condition is apparent here—"What is the use of our trying to do it out here, as they can do it cheaper in the East."

The Pacific Coast possibilities are not only what we find here, but west of here. We have half the world's population facing on the Pacific Ocean, and the consumption of products by these people is continually on the increase. When we realize that during the seventeen years that the Philippine Islands have been under the control of the United States the total imports of those islands have more than quadrupled, it shows that primitive people like the Filipinos, as soon as they can get in touch with

more regulated nations, increase enormously their demand for the products of those nations.

We have Japan and China on the Pacific Ocean to our west. The Chinese as a people are different from the Filipinos, and the possibilities of trade with them are much greater than with the Filipinos, even, and we have other markets which no location in the world is as well fitted to supply as the Pacific Coast.

It might be said at the present time, as we look at it from day to day, that there are very small possibilities in that direction, but that is a very limited viewpoint to take. We are living here today, but others will be living years from now who will take our places. We are building our commerce, not only for ourselves, as individuals, but for a big section of a big country, and we are building also for future generations. Therefore, the attitude to take is the broad man's attitude, to see that we properly lay the foundations, and let the others who come after us put more stones on top of it and finish the structure.

W. E. Herring (*Communicated*): Several additional facts have occurred to me in connection with those brought out in this paper, among which are the following:

The largest single industry in the States of Washington and Oregon is that of lumbering. The amount of absolute waste incurred in this industry is perhaps greater than in any other of the large industries today. Just why some market cannot be found for the immense quantity of waste material is to a certain extent problematical. The by-products consisting of the various oils, acids, tars, etc., are very important in our daily life, and all of them are of special importance to the chemist. Much attention has been paid to this question by the federal government as well as individuals, but so far no answer to the problem has been found.

In the Pacific Coast States it is estimated that there are over 22,000,000,000 tons of coal, of which over 19,000,000,000 tons are found in the State of Washington. A reasonable percentage of this coal is suitable for coke, and while the production of coke at the present time is comparatively small, this is true only for the reason that there is not a greater demand for the material. It can be produced in abundance when the market warrants it.

Iron ores, which are available near the coast in the State of Washington and are found extensively in British Columbia and Alaska, can also be brought into this country from China; in fact, a high-grade Chinese iron ore can be laid down at Pacific Coast points at perhaps a less price than it can be mined in the interior of this country and brought to the coast. One projected industry requiring large amounts of this material on the coast entered into a contract with certain owners in China for iron ore, and the price quoted was but little more than the cost of getting it out, since it was brought over mainly in ballast.

It is estimated that the consumption of fertilizer on the Pacific Coast and in Hawaii is in excess of fifty thousand tons per annum. Much of this is Chilean nitrate, some nitrate imported from Norway and Sweden, and the balance brought in from the southeastern part of the United States. With the rapidly growing use of fertilizer in this country and the extremely low price at which electric power can be had, it is believed that the location of an air nitrate plant of some description on the coast would be well warranted.

The use of the electric furnace is growing, there now being several in operation on the Pacific Coast. In Seattle, one has been operating very successfully for some eighteen months, and two more are building. There is one operating in Portland, with another under consideration, and others are to be found in California. With the grade of steel turned out by the electric furnace, and the price at which it can be produced, there is no question but that it will supersede for many uses the present type of steel casting. With electric current at one-half cent per kilowatt hour and scrap steel averaging eight or nine dollars per ton, there is no reason why the production of this material should not increase very rapidly.

Another very important point in the consideration of location for new industries is that of transportation, and the Pacific Coast is well supplied with these facilities. The populous areas along the coast have many electric and steam railways, these areas being connected by steam roads and also by water transportation lines. Operating out of all of the Pacific Coast ports are steamship lines reaching all points in the world, in addition to the coastwise lines from San Diego to Seattle and from Seattle

to Alaska. One of the most important markets tributary to the Pacific Coast, and particularly to the Pacific Northwest, is Russia. It presents an almost unlimited field for many of our products and is one that up to the present time has been little exploited by the American manufacturer. It is believed that with the close of hostilities in Europe, Russia will prove to be one of our most important consumers.

Government figures show conclusively that the bulk of the potential water power of the United States is west of the Rocky Mountains, and the major portion of this west of the Cascade and Sierra Nevada Mountains. These last two ranges are practically a continuous range paralleling the Pacific Coast line at a distance of one hundred to one hundred and fifty miles and extending from British Columbia to the Mexican line. In the State of Washington the precipitation in the Cascade Range is very heavy, averaging one hundred inches (2.5 meters) per annum. In the mountains there are numerous glaciers and extensive snow fields. The mountain slopes are covered with heavy forests, and the streams have a very rapid fall from their source to within a few miles of the sea. For these reasons it is possible to make power developments at low unit cost, and since no long transmission is required it is possible for the consumer to secure his power at a lower cost than in other portions of the country. In fact, to continuous users of large blocks of power, a lower price is given than can be secured by him today in any other part of the United States.

The construction of power plants has more than kept pace with the demand for power. Up to the past three years it was impossible to supply the existing demand for electric power, but since that time, due to a general depression in business lines and to a more rapid development along power lines, the markets have become saturated, and as a general rule it is not believed that there will be any construction work on new plants of any magnitude until some unusual demand is made for power. In the past few years, too, there has arisen a feeling that a closer regulation of the companies owning and operating the power plants, and more legislation directed at them with the idea of harassing them in many ways, would work to the advantage of the public. With that end in view, apparently, there has been, not only in

this section but in other parts of the country, too much drastic regulation and legislation, with the result that until saner ideas are held by the law-making bodies, it is not believed that new capital will look with favor upon any heavy investment in public utilities.

The remarkable growth of the cities along the coast in addition to the numerous possibilities for expansion along all lines should be proof that this section is thoroughly alive, that it is making rapid strides, and is destined to be a most important part industrially of the United States.

President L. Addicks: The total cost of power consumed, even in electro-metallurgical chemistry, rarely amounts to 20 percent of the cost of operation. I think most people think it is perhaps 50 or 70 percent, and that power is the key of the whole situation. Power, to be sure, is necessary, and it must be cheap, but it is by no means the controlling factor. Then we must remember that even in the vicinity of New York, with quite a reasonably-sized plant, say 10,000 kilowatts, it is possible to generate a kilowatt-hour from anthracite "Buckwheat" coal for 0.3 cent, leaving out overhead expenses, and we must always remember that we have practically 100 percent load factor. There are a great many water powers, even in the West, that will not do much better than 0.3 cent. Then we must remember, most important of all, that any process must be carried to the point where we reach the retail consumer. If we have a copper refining plant, there is no use in making wire bars if there is no market for them here. We must build a rolling mill, wire-drawing plant, and insulating plant, and make the finished article which may be sold on the coast. There is no rolling mill, even in the larger Middle West, at present. When we take these things into account it imposes a very severe handicap in making a success of some of these chemical industries, of which mention was made in the paper, and we cannot figure for a moment bringing materials to make aluminum or any of these products, from any distance, even by water, simply because we have cheap power here. Therefore, I think possibly the paper is a little optimistic in its views, and I hope that we can balance it with a little eastern skepticism.

Gano Dunn: I am loath to rise and possibly be called a skeptic. The Chairman has anticipated the principal part of what I had in mind to say, that too often the glamor of water power is used to carry along with it the prospects of an electrochemical enterprise, which if it could be discussed in the light of just plain power would not have so much attention. Far be it from me to cast any shadow upon the advantages of water power, in which I am deeply interested and upon which depend some of the best interests of the electrical industries in this country, but we must see facts as they are. As matters stand today, water power, whose cheapness is usually urged as the reason why it is to be used for electrochemical industries, is very much on the defensive in large areas of territory. There are some places where water power is so much cheaper than steam power, that it is indicated for electrochemical consideration, but with the prospect of an increase in the rate of interest and the returns that capital will expect, and the coal consumption of steam apparatus, at the decreasing rate of 2.5 percent yearly for the previous decade, notwithstanding an increase in the cost of coal of 1 percent per year for the same period, it looks as if we were reaching a point where, when there are advantages in water power for electrochemical purposes it is due to other considerations than the fact that the power is derived from water.

As the Chairman has stated, it comes down to an argument *pro* and *con* on the basis of load factor, the expenses due to transmission, and the returns due to capital invested, etc. The suitability of water power for electrochemical industries should be discussed not on the basis that the power comes from water, but on the basis that we have here the possibility of 100 percent load factor, with the transmission distances relatively small, and consequently the transmission losses and maintenance charges are removed as a burden on the enterprise.

John H. Finney: Mr. Dunn has just expressed my viewpoint exactly. It is, however, a part of my work to know something about water power. I have been in Washington for a good many years working on the problem and endeavoring to find out what Congress is going to do about permitting water-power development, and I have not found the answer yet. But there exists in Congress, as in many other places when lay discussion is had on

this question, a feeling that the water powers of the United States are tremendously valuable, that every foot of falling water can be developed into power, or, from the Congressional viewpoint, is already power, and that the Water Power Trust named in the report of the Commission of Corporations recently, is going up and down the land acquiring water power rights and taking away from the "people" this tremendously valuable national heritage. That is the attitude at Washington.

They do not realize that the latent power of a stream, even as great a power as Niagara Falls, had never performed a single useful act until money went there and harnessed it up. We have a very large amount of water power in the West, with a present over-development of it if we consider it in its public utility phase, and considerable increase in population and mechanical uses is required to absorb it fully. There, is however, in the West a tremendous amount of water power that will never be used, unless it can be made available as the basis for some electrochemical or electro-metallurgical use. It is too remote from centers of distribution, its market, it costs too much to get it down through long-distance transmission lines, and unless it can be made the basis of a permanent operation, chemical or metallurgical, it will be forever wasted. We are to have a meeting in Portland next week on water power, to see what can be done about straightening the matter out, to see if we cannot get people set right on it. I have a very large interest in doing what I can to help that work along. Water power is valuable only when it is developed, and it takes large amounts of money to develop it. In discussion yesterday, at the Public Utilities session, I expressed my opinion that if returns to capital were going to be limited to a bare 8 percent, as the total return to capital invested in water power, it would be a very long time, in my opinion, before much more water power would be developed on the Pacific Coast. I am naturally an optimist; but I feel if we are going to do anything in the development of water power on the coast or anywhere else in the nation, we must treat the developer more fairly than now seems politically possible, and enact wiser and more adequate laws, if the present waste involved in our policy of stagnation is to be prevented.

President L. Addicks: Doctor Lyon had a paper at our morning session on this same subject, in which he analyzed a number of industries, whether they could be developed or not, and stated his conclusions at length. (See pages 160 and 161.)

In other words, it appears that Doctor Lyon, after considering the present processes, one after another, under local conditions, does not seem to think there is a possibility of their being established, but pins his faith upon unknown development which may come in the West.

C. L. Cory: I have been much interested in the presentation and discussion of this paper. There is no question in my mind, however, that we must consider primarily the economic side in connection with the matter of the utilization of hydro-electric power in chemical industries. I was particularly impressed with what Mr. Finney had to say, and I heartily agree with him regarding the necessary rate of return upon investments in hydro-electric developments, and in this connection beg to draw your attention to some comparisons of the relation of investment and gross revenue that have recently come within my observation.

If you investigate the gross revenue of the principal hydro-electric distribution and transmission systems, you will find that the total annual receipts rarely exceed 25 to 30 percent of the value of the property. Out of the gross revenue must first be deducted maintenance, obsolescence, etc., before the return upon the investment is available.

Let us contrast this situation, if you please, with one of the large corporations in the East, a combination of a number of companies engaged in the business of manufacturing automobiles. The total investment required is approximately $15,000,000. The last annual report shows that the gross sales of this company for the year amounted to $94,000,000. Is it not quite apparent that an adequate rate of return is much more probable in such an organization, where the gross revenue is nearly six times the required investment, than in a hydro-electric development where the gross revenue practically never exceeds a third of the value of the property?

May I introduce another illustration? One reason why a properly developed gold mine is such a desirable industrial project

is because the owners and operators are never concerned about the market for their product. Neither is there concern as to the price which they will receive for this product. But in our public utility enterprises, as well as with the proposed chemical industries, I think we must give careful attention to the varying market prices of the products which are to be sold, especially when the investment required in producing these products is relatively so great.

Contrast, if you please, the large, reliable gold mining enterprises of the world with the iron industries. The reason why the iron industry is so stable, notwithstanding a considerable variation in the market price of the product, is the extraordinarily large demand for the output.

The query which occurs to me relates to the uniform and continuous demand for the product which we shall get from our chemical industries. We can not be guaranteed an unvarying price similar to the price of gold, nor can we feel sure of the demand for our chemical product over the entire world which the steel manufacture enjoys, and I seriously doubt whether the large investment required to produce the electrical energy necessary in such chemical industries, if this electrical energy is to be generated from water power, will be justified until there is an unquestioned market for our chemical products that may be produced upon the Pacific Coast.

This may be only another way of expressing the ideas placed before you by our Chairman, Mr. Finney, Mr. Addicks and also Mr. Dunn.

I recognize, of course, the great desirability in many instances of improving the load factor of existing hydro-electric generating systems. I have in mind one comparatively small hydro-electric property in this State that, on account of a comparatively low load factor, about 60 percent, has been able to deliver from its substation only some thirty-three million kilowatt-hours per year. As a matter of fact this particular system, without any additional expense whatsoever, could have delivered an additional twenty million kilowatt-hours if the demand for power had coincided more nearly with the seasonal supply of water.

Unfortunately we can not get the chemical industries to use such spare power during only the time when it is not used for

other purposes, since it can not be so used economically considering the large investment required in the manufacturing plants of such chemical industries.

The power developments at Niagara Falls, with the very large amount of power there available, would not have been financially successful if the demand for power had been exclusively confined to the chemical industries which were started there as a result of the electrical development of the Falls.

In the small hydro-electric system in this State to which I have just referred, arrangements have recently been made whereby the spare power to the extent of twenty million kilowatt-hours per year has been sold to another company engaged in the same business. It is not difficult to see the advantages of such an arrangement to both companies, since it happens that the variations of load of the two companies, when compared with one another, made it possible to dove-tail very satisfactorily the available amount of power to meet the total power demand.

In connection with hydro-electric development in this State, I personally expect to live to see in the State of California at least one pair of bus-bars extending practically from Siskiyou County to Los Angeles County. These bus-bars will be three-phase, and the voltage on the line will probably be as much as, or even more than, 175,000 volts. Such a pair of transmission lines might well be called, to use a financial term, "clearing house bus-bars," since every hydro-electric development which can be economically utilized should be allowed to deliver its power into such a system, and, on the other hand, wherever power is demanded from one end of the State to the other, it should be taken from these bus-bars.

In this manner there would be produced the best possible composite load factor, and at the same time many possible developments, varying in size from 5,000 to 15,000 kilowatts, will be made available that are not now feasible, since the only markets left for such developments are too far from the sources of power to justify the comparatively long transmission lines necessary.

In conclusion, I think it is well to give careful consideration to what our Chairman has said about the proportion of the total cost represented by the cost of the electrical power required for the development of chemical industries. The comparatively small

cost of the power required I think may be well compared to the cost of fuel used in the ordinary steam locomotive, and of the total operating cost per mile; the fuel cost is but a minor factor.

The more quickly our commissions which are responsible for the regulation of rates thoroughly understand the necessity of making the maximum use of the total kilowatt-hours available, the more quickly will we get a satisfactory working arrangement which will be the best for both customers and public utility enterprises. I am sometimes inclined to think that it is a lack of full appreciation of the real difficulties involved that leads to restrictions that, in the end, will result in the practical elimination of many enterprises which under other conditions would be economically extremely desirable. Too great restrictions in such matters can only result in reducing individual initiative to a negative quantity.

One reason why the development of electrical energy has in the past been such a success is because of the growing demand for kilowatt-hours, and in general the market price has been reasonably stable.

Our chemical industries can only be developed under similar conditions, namely, that there will be an unquestioned demand for the output, and that the market price will not undergo very great variations with changed economic conditions. Until such is the case I feel that the investment of very large sums of money in hydro-electric plants to be used practically exclusively in the manufacture of chemicals is decidedly undesirable.

I had an opportunity a few years ago of learning direct from one of the electrical engineers of Norway many interesting facts regarding the use of electric power there for the manufacture of fertilizer products. I was surprised when he told me that no plant would be justified in Norway in which the total cost, including transmission to the place of consumption, exceeded $40.00 per kilowatt capacity. He further told me that if the electrical energy for such chemical industries exceeded an annual cost of $12.00 per kilowatt, such electrical power could not be economically utilized.

I think you will agree with me that such figures are extraordinarily low, considering the possibilities on the Pacific Coast, and, lest we forget, it might not be amiss to give the most careful

consideration to the present status of the chemical industries in Norway as a result of the European war.

Surely there is no reason to deceive ourselves into thinking that the integrity of the investment in hydro-electric developments on the Pacific Coast to be used almost exclusively for chemical industries can be guaranteed until not only the market but the price of the chemical products which may be produced are both firmly and definitely established.

E. P. Warner: I would like to ask the gentleman what he knows actually in regard to conditions in Norway as to the application of hydro-electric power in the fixation of atmospheric nitrogen. I would also like to ask Mr. Beckman whether some of the sources of power we have are not capable of development at such a low rate that it would be possible to use that power in the fixation of atmospheric nitrogen, as in Norway, and in the manufacture of nitrates, nitrites, sulphuric acid, and various other compounds.

Professor Cory: I will say frankly I know very little of the actual processes in Norway for the fixation of nitrogen. All I do know is the information given to me as to the limitations of the cost of energy for that purpose.

E. P. Warner: We had a paper by Mr. L. L. Summers, of Chicago, not long ago, at a meeting of the American Institute of Electrical Engineers, after he made a visit to Norway, and he gave us a considerable idea as to the development of water power there and the extremely low cost for development. It put the price down to about $8.50 per horsepower for some of the plants, and as low as $5 for two or three of them. It seemed almost incredible, but the main use of these plants, even at those prices, was for the ordinary fixation of nitrogen by the arc method. He described to us two or three of those plants which were being operated with a very small number of employees and were producing very large amounts of nitrogen salts. He showed that they were successful and were doing a large business. He also gave some data regarding the magnitude of the business, and it struck me at the time that in California we had conditions—in fact, all along the coast from the middle of California north clear up into Alaska—where water power can be developed at

very low cost per horsepower; and since nitrogen exists almost everywhere, one of the materials, at least, would be very easy to get. We have also lakes of soda and various other chemicals that are available. It would seem only fair to say that we have perhaps overlooked some of our possibilities.

J. W. Beckman: I want to refer especially to the electrical engineers' point of view as expressed by some of the previous speakers. The electrical engineer is looking apparently on all power developments from the transmission point of view. The electrochemical point of view absolutely disregards transmission necessities. A great number of the large power plants on the coast here are fortunately located either right at tide water or so close to tide water that it is cheaper to manufacture the chemicals at the power site than to transmit the power down to tide water. This eliminates a large investment in transmission line. This is the peculiar advantage which we hold here, and there are only a few countries in the world which have a similar advantage. I believe that New Zealand, Norway and the Pacific Coast are the only locations in the world where cheap power in great quantities can be developed in accessible locations, without necessitating transmitting it to other points for the manufacture of electrochemical products.

As to the nitrogen fixation, I may say that I have looked into that industry considerably, and understand that at present there is close to 300,000, if not 350,000 horsepower, developed in Norway for the purpose of nitrogen fixation exclusively. In one case, 250,000 horsepower is developed for that purpose at a place called Rjukan, in the interior of Norway. There they operate the Birkeland-Eyde process, and produce nitrates, nitric acid and some nitrites.

The present situation in the processes for nitrogen fixation is such that if anybody came to me and asked me if I would advise him to put in a plant for its manufacture I would say "No." In no case are the efficiencies of these processes very great, and in the best of the arc processes 3 percent efficiency is obtained. It is generally considered that 2.5 percent chemical efficiency is the average. I venture to say, without exaggeration, that there are

thousands of people working today in the big plants, and other places, on the problem of increasing the efficiency of the nitrogen fixation process. The cyanamid process, which is not a very efficient process, produces a material that to be of real value in the fertilizer trade has to be changed into ammonia. That is readily done by treating the product with steam, but this entails an additional cost.

I have looked quite considerably into the power development possibilities and cost of power on the Pacific Coast. The Chairman has told me I am an optimist. It is a good thing sometimes to be an optimist, especially among electrical engineers, I find. The cost of power here is low. At the projected development at Dalles, Oregon, blocks of power have been offered at less than $10 per horsepower-year. There are large projected developments on the coast, I am informed, ready to supply power at less than $5 per horsepower-year, provided large blocks are taken. I believe we have indeed a very unusual situation here, which with few exceptions is not equaled in any place in the world, and the West Coast of the United States is going in time to become one of the electrochemical centers of the world.

E. Bruce Pratt (*Communicated*): Mr. Beckman states that the thought that Pacific Coast power is prohibitive in price is erroneous; that "power can be obtained close to the generating stations as cheap, if not cheaper than, the prices generally quoted for power at Niagara Falls," etc.

The writer has recently obtained prices from all the large power companies in California, including the Great Western Power Co. with which Mr. Beckman is connected, these quotations being for large quantities of power for the electrical reduction of iron ore by the Pratt process, patent for which was allowed on June 19, last, and demonstration of which is now being conducted in Cleveland, Ohio.

These quotations covered both continuous and "off-peak" load. The best prices obtainable were in the approximate neighborhood of one cent per K. W. H. for continuous current and half a cent per K. W. H. for "off-peak" load.

The prices obtainable at Niagara Falls and vicinity, including

Canadian territory, are approximately one-fourth cent per K. W. H. for continuous current, while some contracts made when the power at Niagara was first developed give power at one-eighth cent per K. W. H. and can be taken over today at that figure.

It is well known that many water powers can be developed at a cost to make it possible to sell power in larger quantities for $15.00 per K. W. Y. It is natural for the power companies to get as much for their power as possible, a fact, which, as my experience proves, will make it necessary for electrochemical industries desiring to locate on the Pacific Coast to own their own water power.

J. W. Beckman (*Communicated*): I would like to take issue with Mr. Addicks as to the influence of the cost of power on the total cost of manufacture, in electrochemical and electro-metallurgical industries.

The following table shows what percentage the power cost is of the total cost of production of various iron alloys, pig iron and caustic soda.

The information regarding the pig iron and alloys is from Mr. Dorsey A. Lyon's reports "Electric Furnaces for Making Iron and Steel," and "The Electric Furnace in Metallurgical Work."

	Cost of power per K. W. Y.	Power cost, percent of total cost.
Ferro Silicon	$26.66	35.2
Ferro Chrome	26.66	24.5
Electric Pig Iron	7.5	24.0
Caustic Soda	40.	25.0

From this it is apparent that in these industries Mr. Addicks' 20 percent is too low, and I believe that in a great number of electrochemical industries the cost of the power will be closer to 30 percent of the total manufacturing cost than Mr. Addicks' figure.

Mr. Bruce Pratt's statement as to cost of power on the Pacific Coast is correct as far as it goes, and I think Mr. Pratt has done well to obtain as good quotations as he has for power. But it is only correct to the extent of being even a very doubtful indication as to what the power companies would do if they really got down to business.

I can state with assurance that the Great Western Power

Company is not only willing but prepared to give "off-peak" power at prices that cannot be equaled excepting by some of the earliest contracts in Niagara Falls, made before the modern power plants were there.

As to 24-hour power for any electro-metallurgical industry desiring to locate here, the Great Western Power Company is prepared to offer power at tide water at prices fully as low as that at which power is obtainable in Niagara Falls today.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

HEAT LOSSES FROM AN ELECTRIC STEEL FURNACE.

By W. H. Wills and A. H. Schuyler.

The furnace investigated is at the plant of the Treadwell Engineering Company, Easton, Pa., and has been already described in these Transactions (1914) **25**, p. 133, where a full description of the furnace may be found. The furnace is of the Heroult type of two-ton rated capacity, with magnesite brick hearth overlaid with burnt dolomite. The pouring spout is in the center of the front side and at each side is a charging door. Three cylindrical graphite electrodes 8 inches (20 cm.) in diameter pass through the roof, threaded for continuous feeding, and are used in 180 pound (82 kg.) sections three feet (90 cm.) long. The power supply is 400 kw., 3 phase, 60 cycle, alternating current, the potential between the electrodes being 80 volts and the normal current per phase 2,500 to 3,000 amperes. The Easton Light and Power Company furnishes the current, at 11,000 volts on the primary.

The object of the experiments was:

I. To investigate the heat losses due to gases issuing from charging doors and tap holes.

II. To investigate the heat losses by conduction into the electrodes and by the water jackets surrounding the electrodes.

Average Operating Conditions.

The product is high grade steel castings, carbon 0.05 to 1.20. Raw material, boiler punchings and structural steel scrap. Lime and some hematite are charged as flux, with fluorspar later. Coke dust is added toward the end of the run, to deoxidize the slag. Final additions of ferro-manganese, ferro-silicon, and aluminium are made. The average length of the heat is 4½ hours. Elec-

trode consumption per heat (2 tons) about 60 pounds (27 kg.); per ton of steel 30 pounds (13.6 kg.); per kw. hour 0.0375 pound (17 grams). The average power input during the test was 350 kw.

I. HEAT LOSSES THROUGH ESCAPING GASES.

Sheet iron flues to facilitate collection of the issuing gases and their measurement were fitted to the furnace doors and tap-hole. The one for the charging doors had a 6-inch pipe, and the one for the tap-hole a 3-inch pipe. The temperature of the escaping gases was measured as they issued by a LeChatelier thermocouple, protected by asbestos tubing. The temperature of the gases leaving the pipes, where the velocity was measured, was taken by suitable mercury thermometers. The velocity of the gases issuing from the 3-inch pipe was measured with 2½-inch (6 cm.) anemometer and on the 6-inch (7.5 cm.) pipes and with a 6-inch anemometer. An Orsat apparatus was used to analyze the escaping gases.

On the first test, run April 16, 1915, the length of the run was four hours twenty-five minutes. The sheet iron flues were placed over the charging door openings and tap hole, and carefully plastered around with fire clay. The following observations were taken at approximately equal intervals:

1. Temperature of gases escaping through the door and tap hole.
2. Temperature of gases leaving pipes.
3. Velocity of gases leaving pipes.
4. Power input to the furnace.
5. Sample and analysis of furnace gases.
6. Barometer reading.

In taking the temperature of the escaping gases, the hot junction of the thermocouple was placed at different points in the openings, and an average reading of the temperatures of gases escaping was obtained.

The following table gives a general log of the observations taken:

TABLE I.

Time	Initial Temperature of Gases, C°	Temperature of Gases leaving Pipes, C°	Velocity of Gases leaving Pipes		
			Feet per Minute	Meters per Minute	Power Input, Kw.
12:30	Furnace charged.				
1:30	door 1.....745	215	310	80	300
	door 2.....755	158	340	86	
	tap hole.....716	202	300	76	
2:00	door 1.....755	230	295	75	390
	door 2.....723	142	290	73	
	tap hole.....735	312	240	61	
2:30	door 1.....774	242	335	85	390
	door 2.....784	117	290	73	
	tap hole.....735	256	260	66	
3:00	door 1.....842	255	320	81	350
	door 2.....832	110	256	65	
	tap hole.....745	230	300	76	
3:15	door 1.....866	265	334	85	360
	door 2.....804	108	260	66	
	tap hole.....876	192	288	73	
3:30	door 1.....903	270	325	82	350
	door 2.....850	110	245	62	
	tap hole.....920	235	292	74	
4:00	door 1.....1000	282	350	89	350
	door 2.....929	115	250	64	
	tap hole.....973	195	300	76	
4:30	door 1.....1018	210	370	94	370
	door 2.....964	112	255	65	
	tap hole.....1010	203	284	72	
5:00	Furnace tapped.				

TABLE II.

Analysis of Gases.

Time	Opening	CO_2	O_2	N_2
1:30	door 2	3.6	18.6	79.2
2:00	tap hole	11.8	9.4	78.8
2:30	door 2	0.4	20.2	79.4
2:50	tap hole	5.0	16.9	78.1
3:15	tap hole	3.0	18.1	78.9
4:00	door 1	3.2	14.9	81.9

TABLE III.

Heat Losses.

Time	Opening	Corrected Vol. Escaping Gases per Minute, Cubic Meters	Temp. C°	Calories Lost per Minute	Kw. Lost	Total Loss, Kw.
1:30	door 1	1.1	745	273.5	19.07	44.4
	door 2	1.216	755	304.8	21.25	
	tap hole	0.247	716	58.4	4.08	
2:00	door 1	0.932	755	245.3	17.10	40.00
	door 2	1.093	723	274.0	19.12	
	tap hole	0.202	735	54.1	3.78	
2:30	door 1	1.006	774	256.7	17.9	41.8
	door 2	1.162	784	796.1	20.65	
	tap hole	0.194	735	46.4	3.24	
3:00	door 1	0.941	842	267.5	18.62	39.00
	door 2	0.832	832	233.	16.27	
	tap hole	0.233	745	58.1	4.06	
3:15	door 1	0.961	866	277.8	19.38	44.40
	door 2	0.073	804	288.1	20.10	
	tap hole	0.242	876	70.7	4.93	
3:30	door 1	0.930	903	288.9	19.64	44.40
	door 2	1.010	850	285.3	19.92	
	tap hole	0.225	920	69.4	4.84	
4:00	door 1	0.975	1000	329.9	23.00	50.85
	door 2	1.014	929	316.7	22.10	
	tap hole	0.251	973	82.4	5.75	
4:30	door 1	1.180	1018	406.9	28.37	57.50
	door 2	1.038	964	337.7	23.55	
	tap hole	0.234	1010	80.00	5.57	

II. ELECTRODE HEAT LOSSES.

The furnace was provided with three electrodes passing through the roof of the furnace, each being in sections of about three feet long and weighing 180 pounds per section (82 kg.). In the electrode holders electrical connection is made by copper plates screwed fast against the graphite and connected to the bus bars by heavy stranded copper cables.

The tests on electrode heat losses were run on April 17, 1915, from 9:35 A. M. to 1:35 P. M. Two chalk marks were made on each electrode between the water jacket and the electrode holder. The temperature of the incoming and outgoing water for the

electrode water jackets was measured with ordinary thermometers.

The following observations were taken every half hour:

1. Temperature on the electrode surface at each chalk mark.
2. Power input to the furnace.
3. Current passing through each electrode.
4. Temperature of cooling water entering and leaving water jackets.
5. Rate of discharge of cooling water.

The temperature of the electrode surface was taken by a thermocouple pressed by a small piece of asbestos tightly against the surface of the electrode. From these observations the calories carried away from the electrode by the cooling water and by conduction through the electrodes could be calculated, using the heat conductivity of graphite for the range of temperature observed.

Table IV contains the record of water entering and leaving the cooling jackets and its quantity.

TABLE IV.

Log of Cooling Water.

Time	Cooling Water			
	Entering C°	Leaving C°	Quantity per Minute Lb.	Kg.
9:45 A. M.	8.5	17.5	42	19.05
10:40 A. M.	8.5	15.5	42	19.05
11:05 A. M.	8.5	16.0	42	19.05
11:30 A. M.	8.5	19.0	42	19.05
12:00 M.	8.5	20.5	40	18.15
12:30 P. M.	8.5	23.0	40	18.15
1:00 P. M.	8.5	25.5	42	19.05
1:30 P. M.	8.5	26.0	42	19.05

Furnace charged at 9:35 A. M.
Furnace poured at 1:35 P. M.

Table V shows the reduced values of heat losses in cooling water per minute at each of the 8 observations.

TABLE V.

Heat Loss in Water Jackets.

Time	Calories per Minute	Kw.	Power Input	Percentage Energy Loss
9:45	171.45	11.95	200	5.97
10:40	133.35	9.3	360	2.58
11:05	14.28	9.97	375	2.66
11:30	200.	13.95	350	3.99
12:00	217.8	15.18	400	3.80
12:30	263.4	18.38	300	6.13
1:00	324.	22.6	300	7.53
1:30	334.	23.3	310	7.50

Average 5.20

In Table VI t_1 is the temperature at the upper chalk mark, t_2 the temperature at the lower chalk mark, and the next column gives the difference in temperature in centigrade degrees, for each of the three electrodes, at the times given.

TABLE VI.

Temperature Observations on Electrodes.

Time	Electrode No. 1			Electrode No. 2			Electrode No. 3		
	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1	t_1	t_2	t_2-t_1
9:45 A. M.	208	293	85	230	304	74	230	304	74
10:40 A. M.	227	293	66	230	293	63	241	329	88
11:05 A. M.	241	316	75	241	293	52	251	329	78
11:30 A. M.	251	328	77	230	293	63	241	328	87
12:00 M.	251	328	77	241	305	64	251	334	83
12:30 P. M.	230	294	64	241	305	64	209	316	107
1:00 P. M.	241	305	64	251	328	77	262	360	98
1:30 P. M.	230	305	75	209	294	85	230	328	98

Table VII was calculated using the following data:

Cross section of each electrode 50.265 square inches (324 sq. cm.). Length of electrode between observation points, as follows:

	Electrode No. 1	Electrode No. 2	Electrode No. 3
9:45 A. M. observations	8 inches (20 cm.)	7 inches (17.5 cm.)	7.5 inches (18.5 cm.)
Other observations	4.87 inches (12.2 cm.)	4.87 inches (12.2 cm.)	5.25 inches (13.1 cm.)

Electrical resistivity of the graphite assumed 0.0003325 ohms per inch cube.

Thermal conductivity of graphite assumed 3.71 watts per inch cube.

These values were assumed as average values for the range of temperature concerned.

From these data calculations of the flow of heat in kilowatts were made according to the methods of Carl Hering, Transactions of the American Institute of Electrical Engineers (1910) **29**, 485, with the following results:

TABLE VII.

Time	Electrode No. 1, Kw.	Electrode No. 2, Kw.	Electrode No. 3, Kw.	Total Kw.	Power Input Kw.	Percentage of Power Input
9:45	1.221	1.918	1.783	5.622	200	2.81
10:40	2.412	2.281	3.011	7.704	360	2.14
11:05	2.775	1.894	2.612	7.261	375	1.93
11:30	2.855	2.229	2.874	8.019	350	2.32
12:00	2.805	3.237	2.813	7.945	400	1.99
12:30	2.344	2.677	3.370	8.441	300	2.81
1:00	3.367	2.876	3.403	8.646	300	2.88
1:30	2.784	3.171	3.403	9.358	310	3.02

Average 2.10

The following table gives the rate of total electrode loss, by cooling water and by conduction through the electrodes, and its percentage of the power input of the furnace:

TABLE VIII.

	Cooling Water, Kw.	Electrodes, Kw.	Total Kw.	Power Input, Kw.	Percentage Loss
I	11.95	5.622	17.572	200	8.79
II	9.30	7.704	17.004	360	4.75
III	9.97	7.261	17.231	375	4.60
IV	13.95	8.019	21.969	350	6.26
V	15.18	7.945	13.125	400	5.78
VI	18.38	8.441	26.821	300	8.94
VII	22.60	8.646	31.246	300	10.42
VIII	23.30	9.358	32.658	310	10.53

Average 7.30

GENERAL REMARKS.

Both tests were run when the furnace was in good operating condition, for a new lining had been put in the day previous to the first test.

The door heat-loss measurement was by far the most difficult, owing to the necessity of handling the hot flues and fitting them tightly over the door openings. Several factors combine to vary the amounts of gas escaping through the different doors. Chief among these is the direction of the air currents through the foundry. Thus, during the latter part of the run a noticeable draft was blowing toward the right-hand charging door (No. 2) so the volume of gas escaping through this door was reduced while a corresponding increase was produced in the volume escaping from the tap hole (No. 3) and especially in the volume escaping from the left-hand charging door (No. 1). These changes are clearly shown by the gas volumes issuing from the different doors.

Each time flux was added to the bath the gas volume was appreciably increased for several minutes while flames shot out through the door openings. Just after the furnace is charged the gas volume is greater, due to the driving off of moisture and other volatile constituents of the charge and to the combustion of oil on the scrap steel. This probably accounts for the high heat loss through the doors at the beginning of the run.

As shown by the tables the loss increased toward the end of the run, being a maximum at tapping time. This is perfectly natural, for it is at that time that the furnace temperature is a maximum.

There is comparatively little gas generated in the simple melting-down operation. It was observed that a considerable portion of the furnace gases must be supplied by cold air flowing in under the charging doors through the opening between door and sill, where an appreciable in-draft was noticed. The furnace thus has to heat up this unnecessary air and then discharge it at a high temperature through the openings at the top of the charging doors and tap hole. This means lower efficiency.

The charging-door loss could be reduced very materially by making the doors fit closely against the furnace walls so as to

cut off as much as possible the air flowing in at the bottom and the outgoing gases through the opening at the top. In the design of subsequent furnaces of this type two methods could be employed to accomplish this result:

First: By the use of a round charging door in the form of a plug mounted to swing on vertical trunnions. This does away with counter weights and permits the door being made thick enough to reduce leakage to a small amount.

Second: By having the furnace walls slightly inclined inward at the charging door ends and using vertically sliding doors with counter balance. The pull of gravity would then hold the doors with sufficient firmness against the walls.

The electrode heat loss is a necessary evil. Of course, the more electrodes through the roof the greater this loss amounts to, so the only way to minimize this loss on a small furnace is to run on single phase. Graphite electrodes were used on this furnace, which means a higher heat loss than with amorphous carbon electrodes.

The high electrode loss at the beginning was due to the fact that the electrodes, which were very hot from the previous heat, had been raised up to allow for the new charge, so that the surface ordinarily well below the water jackets was exposed and the portion next to the water jackets was red hot. This made the surface temperatures at first higher than they would be if the furnace was started cold. As the furnace temperature rose toward the end, the electrode loss naturally rose. This rise was more noticeable in the heat carried off by the cooling water than in that traveling up the electrode by conduction. The temperature at the two marks on each electrode did not change as much as might be expected, because the electrodes, after being pushed a maximum distance down into the bath when the charge was first melted down, were gradually withdrawn, so that the marks rose higher and higher above the water jackets. If the furnace temperature had remained constant, the surface temperature at the marks would have fallen.

The formulas used in calculating the heat passing out through the electrodes depend on the assumption that the electrodes have uniform cross section throughout their length, that the conduc-

tivities for heat and electricity are linear functions of the temperature, and neglect the loss by radiation from the electrode surface between the points at which the temperatures were taken. Since the distance between these points was comparatively small this radiation loss amounted to very little. The electrodes were uniform in cross section throughout.

The heat carried off in the water from the electrode water-jackets is not all from the electrodes, but a considerable part is from that part of the roof adjacent to the electrode openings. However this loss is made necessary by the electrodes and so may be counted under the head of electrode losses.

CONCLUSION.

By integrating the door and electrode loss curves and dividing these areas by their length, the average door and tap hole loss was found to be **12.5** percent and the electrode loss **7.3** percent of the power input to the furnace. The electrode loss can not be cut down much so long as graphite electrodes are used, but the door loss can be reduced a considerable amount by making the charging doors fit closely against the furnace walls, and the tap hole loss reduced by suitable closing devices.

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DISCUSSION.

Carl Hering (*Communicated*): Those who are dealing with electric furnaces are naturally always interested in experimental determinations. Facts are always more useful than theories. The data in this paper are therefore of interest because they are empirical.

Measurements as those described, however, are necessarily so crude and inaccurate that too much reliance should not be placed on them. The errors in the deductions from such tests may be very great, possibly even in some cases reaching 100 percent.

It is not clear why quite a stream of gases should come out of a "tap hole" which is only opened when the furnace is tapped,

and it is always below the level of the molten liquid. It is not at all clear where the water jacket is placed on the electrodes, as it is evidently not a part of the electrode holder, as is usual. Moreover it is not clear why the heat traveling up through the electrodes should be added to that found in the water jacket, for if the water jacket is placed on the electrode as is apparently the case, the heat reaching it must of course pass up through the electrode.

The calculation of heat losses traveling up through the electrode in the way they describe, it seems to me, must necessarily be very crude. The loss through the electrodes (as measured by them) is not properly comparable directly with the input of power at that moment, at it must vary greatly with the previous history of that run, that is, whether the input or the temperature was rising or falling at the time. The specific heat of such large electrodes would presumably also cause a very great lag. To take the average of several readings is not altogether correct when the individual readings vary several hundred percent from each other, nor is it correct at all unless the readings are equally spaced in time.

That the heat losses through the electrodes must necessarily be greater when graphite electrodes are used than when they are carbon, as stated by the authors in the middle of page 215, is by no means necessarily true; in fact, when they are correctly proportioned (if it becomes physically possible to do so, which is not always the case) the reverse is generally the case; it is well known that heat conductivity is not the only criterion in determining electrode losses. Their graphite electrodes were probably unnecessarily large.

The entrance of cold air into an electric furnace, causing a draught of air through it, should be most carefully avoided in good furnaces, as it is a robber of heat of the worst kind.

President L. Addicks: I was figuring over the data given in connection with these two furnaces, one of which consumes 1,780 kilowatt hours per ton of metal; and the gas losses are given at 99 kilowatt hours per ton of steel produced, which would seem enormous. It occurred to me that the method of measuring the

escaping gases created a draught which acted as a chimney and increased the escape of the gas.

I would like to ask Dr. Richards whether they were forcing leakage which did not normally exist, by putting on the chimney.

SECRETARY J. W. RICHARDS: There may be something in that suggestion. In order to determine the velocity of the gases visibly escaping, they put a little hood over the door to collect them and a short pipe to lead them away. That would increase the amount of circulation of the gases.

I think there is no doubt that the draught was to some extent artificially increased, but while they may have exaggerated the amount of loss, yet it is a much larger item than it is usually thought to be. And a small circulation of air in and out of the furnace is a thief of the worst kind, as Mr. Hering says.

I have seen electric furnaces running with the tap hole or pouring spout open, and I am sure that a considerable percentage of the whole furnace energy was being taken away, in addition to the great consumption of the electrodes which it caused. One furnace I have in mind had originally four charging doors, and one tap hole. They had closed two of the doors permanently, but the other two were poorly fitted. There was a draught of air sucking in at the doors and the pouring spout, and going out of the gaps around the electrodes, which must have been wasting energy enormously.

While the figure given by Wills and Schuyler is high, I think it is below some of the losses incurred by air circulating into and out of some furnaces, and I think the designers of electric furnaces who are making close-fittings around the doors and the pouring spouts are working in the right direction.

A. M. WILLIAMSON: There is one point which should be borne in mind in connection with this paper, and that is that the losses due to heat conductivity of the electrodes could be reduced to a large extent by using a smaller electrode. In the case in question the electrodes are considerably larger than would ordinarily be recommended considering the current used, and it is apparent that the heat conducted away by say a 6-inch (15 cm.) electrode would be much less than with the 8-inch (20 cm.).

This should not be taken as a criticism of the practice of the company operating the furnace, for sometimes other factors enter into the commercial operation of furnaces which make is impractical to follow the practices which are best theoretically.

PRESIDENT L. ADDICKS: You balance the C^2R losses against the conductivity losses?

A. M. WILLIAMSON: The usual commercial practice is to take as full advantage as possible of the high electrical conductivity of the graphite electrode.

PRESIDENT L. ADDICKS: Is this a commercial furnace?

SECRETARY J. W. RICHARDS: This is a commercial furnace making steel castings for the last three or four years, and to the great satisfaction of the people running it. I think some of the points raised by Dr. Hering will be answered by the authors, but some might be answered here: Mr. Hering misconceives the idea of where the heat losses through the electrodes are taken. They were taken above the water jacket. The heat losses above through the body of the electrode, are to be added to the heat loss through the water jacket. Mr. Hering objected to them being added together.

W. H. WILLS, JR. (*Communicated*): A stream of gases was always issuing from the "tap hole" or pouring spout of the furnace because it was only partially closed with a silica brick during the melting operation. Originally there had been a door for the "tap hole," but it had been removed for a long time.

I probably should have stated the location of the water jackets for cooling the electrodes. These, as shown in the illustrations of our original thesis, rested on the roof of the furnace and surrounded the electrodes where they entered the openings in the roof. Therefore the adjacent parts of the roof as well as the electrodes imparted heat through the jackets to the cooling water. Of the total heat passing out from the interior of the furnace through the electrodes a considerable portion is given off to the water jackets on the outer surface of the roof, but a larger part travels on up through the electrodes by conduction and is disposed of either by radiation to the air or by conduction to the electrode holders. The observations for calculating the heat

passing up through the electrodes were made on the surface of the electrodes above the water jackets and between them and the electrode holders. Dr. Richards conveyed the right idea of this to Dr. Hering in his discussion.

The heat loss through the graphite electrodes which were used on the furnace was somewhat more than would have been the case if amorphous carbon electrodes had been used, owing to their higher thermal conductivity. On the other hand graphite electrodes have the advantage of being better electrical conductors, which more than offsets the disadvantage of being better thermal conductors.

In my opinion, the flues which we used for measuring the escaping gases did not appreciably affect the volume leaving the doors. Any draught which was created would probably be neutralized by the friction of the gases passing through the curved pipe and parts of the flues of reduced cross section.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

ELECTRIC STEEL COSTS.

By F. T. Snyder.*

It is now widely known that steel of high quality can be made electrically. It is known to a considerable number of metallurgists that properly designed electric furnaces will operate reliably and regularly with a lower percentage of lost time than a fuel furnace of equal output. It is convincingly known to only comparatively few makers of steel that electric steel can be made at a cost substantially below the corresponding cost with fuel furnaces. These few naturally include the operators of the furnaces that are making such records.

To render this information more widely available, this paper gives the operating costs for two sizes of furnaces in common use and of a type designed by the writer. In each case the costs represent records extending over continuous commercial use for periods of from one and a half to two years. As these costs are markedly lower than records of similar character of earlier types of electric steel furnaces, some of the reasons are given why such lower records should be expected with this latter furnace design.

This style of furnace from which these operating costs were obtained, is shown by this diagram. (Fig. 1.)

The furnace consists of a circular shell lined with refractories. The current enters at A at the bottom of the crane and passes into the furnace by a single electrode E in the center of the furnace. The heat is generated in the arc by which the current jumps from the electrode to the slag covering the metal. The electric current leaves the furnace at C through a contact with the metal bath.

* Snyder Electric Furnace Co., Chicago.

These operating costs as given do not include supervision, as the amount involved is so small, due to the simplicity and reliability of these particular furnaces, that no additional cost to the plants containing these furnaces resulted on account of such supervision.

No overhead, due to cost and maintenance of buildings, is included in these costs, as the intention is to make these records of use to prospective users of such electric melting furnaces, and

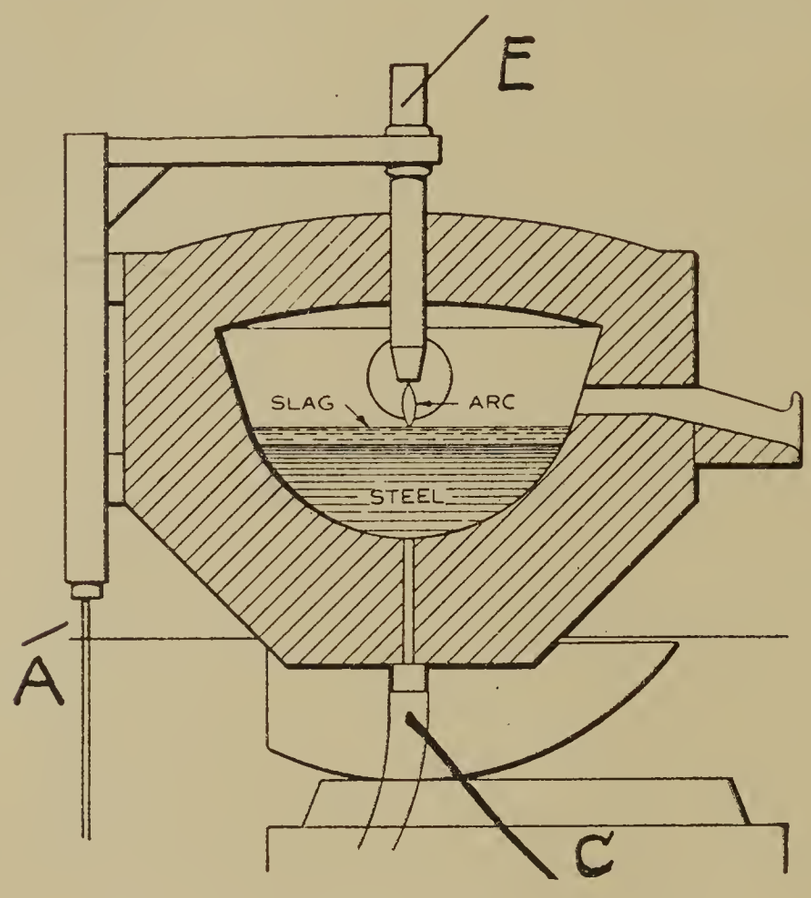

Fig. 1. One Electrode Type Steel Furnace.

the building overhead cost varies widely from plant to plant, and is substantially independent of the sort of furnace used. The metal loss, due to spills and oxidation, is not included, as these depend largely on the care used by the melter. In each of the furnaces from which these costs come, the metal loss has been substantially below 1 percent of metallic contents of the charge. The cost for scrap used are real prices over long periods of time for special scrap material, and are due to the ability of these electric furnaces to handle low-priced material.

In comparing these operating costs with other published records, it should be kept in mind that these costs do not represent single heats, or runs made under test conditions, or under exceptional circumstances. These costs are the average of regular commercial operation during long continued industrial service. These costs include the stand-by losses between heats, the breakages and waste of supplies, the lost time on Sundays and holidays, the overtime work on maintenance.

ELECTRIC STEEL MELTING.

Costs of Operation When Melting Cold Scrap at 10-Ton Output.

		PER DAY	PER TON
OUTPUT:			
Heats in 11 hours		4	
Tons of metal in 11 hours		10	
LAROR:			
Melter	$4.00		
Helpers	2.50		
		$6.50	$0.65
ELECTRICITY (per kilowatt hour 0.7c.):			
Furnace	34.70		
Substation	4.00		
		38.70	3.87
SUPPLIES:			
Refractories	3.00		
Electrodes	6.00		
		9.00	.90
MAINTENANCE:			
		2.40	.24
Direct cost		$56.60	$5.66
BURDEN:			
Interest, depreciation and taxes		18.00	1.80
Conversion cost		$74.60	$7.46
CHARGE:			
Scrap	$110.00		
Alloys	6.00		
		116.00	11.60
Total cost melted metal		$190.60	$19.06

COST OF ELECTRIC STEEL.

Costs of Operation When Melting Cold Scrap at 6-Ton Output.

		PER DAY	PER TON
OUTPUT:			
Heats in 12 hours		4	
Tons of metal in 11 hours		6	
LABOR:			
Melter	$3.00		
Helpers	1.40		
		$4.40	$0.74
ELECTRICITY (per kilowatt hour 1.4c.):			
Furnace	45.02		
Substation	1.84		
		46.86	7.81
SUPPLIES:			
Refractories	1.70		
Electrodes	3.00		
		4.70	0.78
MAINTENANCE:			
		.84	0.14
Direct cost		$56.80	$9.47
BURDEN:			
Interest, depreciation and taxes		11.30	1.88
Conversion cost		$68.10	$11.35
CHARGE:			
Scrap	$58.00		
Alloys	2.04		
		60.04	10.01
Total cost melted metal		$128.14	$21.36

While these costs are taken directly from long continued industrial operations, they are so low compared with similar records for furnaces of earlier design, that they naturally do not carry immediate conviction to operators who have had direct access to similar records of such earlier furnaces. It is desirable to show in some detail why such low operating costs should be expected with this type of furnace.

Considering the cost items in the reverse order from that in which they appear on the cost statement, the item of burden, which includes interest, depreciation and taxes, is low due to the rapid melting ability of these furnaces. Each of these furnaces

has regularly made four heats in an eleven-hour shift. This is about double the output for the size of furnace of that from furnaces of earlier design, and the burden item per ton of output is therefore correspondingly reduced.

The item of supplies is made up of electrodes and refractories. Each of these furnaces runs regularly on less than four pounds of electrode per ton of steel poured, as compared with an average of thirty pounds for furnaces of earlier design. This large difference is due to the joint operation of several causes. The most important of these is the use of a single electrode in place of three electrodes. Electrode consumption is largely a matter of surface burning. Three electrodes of the same size would naturally burn three times as much as a single electrode. Actually, the ratio is much higher than three to one for the following reasons:

The highest permissible voltage that can be used is determined by considerations of safety to furnace operator. With a three-electrode furnace the voltage between electrodes is 173 percent of the voltage from each electrode to the bath. Due to the extra heat losses with a three-electrode furnace the total energy to be introduced through the electrodes for the same tonnage output per day is about 150 percent of the energy required with these single-electrode furnaces. This lower arc voltage and consequent larger current to be carried, and the larger input, result in three electrodes for the three-electrode furnaces each as large as the single electrode of these one-electrode furnaces, if made of the same material. Electrode cost is made up of two items: The heat lost through the electrode during its life and the original cost of the electrode. In commercial operation in this country cost conditions are such that the higher consumption with the three electrodes makes the first cost the prime consideration. It is more economical with three electrodes to use amorphous carbon, and more economical with a single electrode to use graphite. Amorphous carbon has a lower current carrying capacity than graphite and this, with the lower voltage permissible with equal safety, results, with good engineering, in three electrodes each about twice the diameter of the single electrode; thus exposing six times the area of surface to burning with the same tonnage output. In addition amorphous carbon burns more readily than

graphite, so that the actual ratio from practice of from eight or nine to one for the relative electrode consumption of a single- and three-electrode furnace is what should be expected.

Most of the refractory wear in an electric furnace is on the roof. The sides are banked up with relatively cheap material that keeps the walls from wearing. This roof wear is largely around the electrodes and is partly due to the hot gases that escape between the electrode and the roof. With three electrodes this wear of the roof near the electrode would be expected to be three times as large with a three-electrode furnace as with a one-electrode furnace. It is further increased due to the fact that three-phase current is used with three electrodes. This gives a difference of potential between electrodes 73 percent higher than the potential from each of the three electrodes to the bath. Fire-brick at steel melting temperature is a relatively good conductor of electricity, having a resistance of about one ohm per inch cube.[1] Consequently, a considerable current flows between electrodes through the hot roof material. This current flow further heats the roof just as the current heats the filament of an incandescent lamp, and heats it just at the places where the roof is already at the highest temperature. To reduce this leakage current between electrodes, the electrodes of a three-electrode furnace are moved as far apart as practical. The further they are moved apart the nearer the arcs come to the walls and the higher the cost of wall refractories per ton of product. With these single-electrode furnaces, the arc is at the center at the maximum distance from the walls, with consequent low wall wear.

With equal safety to operators, the arc voltage of a single-electrode furnace is substantially double that of the voltage of each arc of a three-electrode furnace. The length of an arc under steel melting conditions increases rapidly with increase of voltage. The temperature of an arc in a steel furnace is determined by the amount of energy it has to radiate per square inch, substantially according to Stefan's law. With these single-electrode furnaces the energy consumed is low, and the arc surface is large. Therefore the arc temperature is low.

[1] Extension of curve of data given by A. Stansfield: Trans. Am. Electrochemical Soc., 22, 93 (1912).

The refractories are at a temperature between the arc temperature and the temperature of the bath, as in an arc furnace about 50 percent of the energy reaches the bath by reflection from the lining of the furnace. Therefore, the lower arc temperature of these single-electrode furnaces means a lower refractory temperature. At steel melting temperatures even a few degrees' drop means a large extension of the life of the refractories, so that it should be expected that with these furnaces with low temperature arcs the refractory costs should be low.

The electric heat used in an electric steel melting furnace is made up of two parts. One part goes into the metal and goes with the metal into the ladle. This part is a fixed amount per ton for a definite pouring temperature. It is the same for all steel melting furnaces, both fuel and electric. The other part represents the heat lost during the melting operation. It all appears in the heated air around the furnace or in the cooling water from the various jackets used. This heat is lost through the doors, the roof, the shell and the electrodes.

These furnaces are fitted with a door in the form of a plug (Fig. 2), so that in place of the usual 4½-inch (11.5 cm.) of door brick, they present the resistance of 14 inches (35 cm.) of thickness to the flow of heat. Thorough tests of the sliding type of door usually used with earlier furnaces show a door loss exceeding 100 kilowatt-hours per ton of steel. Much of this is saved by this plug type of door. We have no experimental results on the actual heat losses with the plug type of door, but our calculations, based on its outside temperature, show probable heat losses of 3.3 K.W. per furnace door.

These furnaces have roofs substantially 50 percent thicker than those of earlier design. Special attention has been given to the design of the shell linings of these furnaces, which are made up of a series of concentric refractories, each proportioned for its specific part of the heat insulation work. They are designed for and operate with external surface temperatures at about 60° C. It is practical to hold the hand against the outer surface of the shell of these furnaces. In actual practice the radiation losses are so low with these furnaces that no extra means are used to keep them hot between heats. With furnaces of older design it is usual to keep current on at reduced input, or to use

an oil burner during the off-shift when a furnace operates only one shift a day. With these furnaces, which both operate eleven hours a day only, no electricity or oil is used on the off-shift. The furnaces are luted up after the last heat of a shift and when opened for the next day's operation have lost so little heat as to be ready for immediate operation.

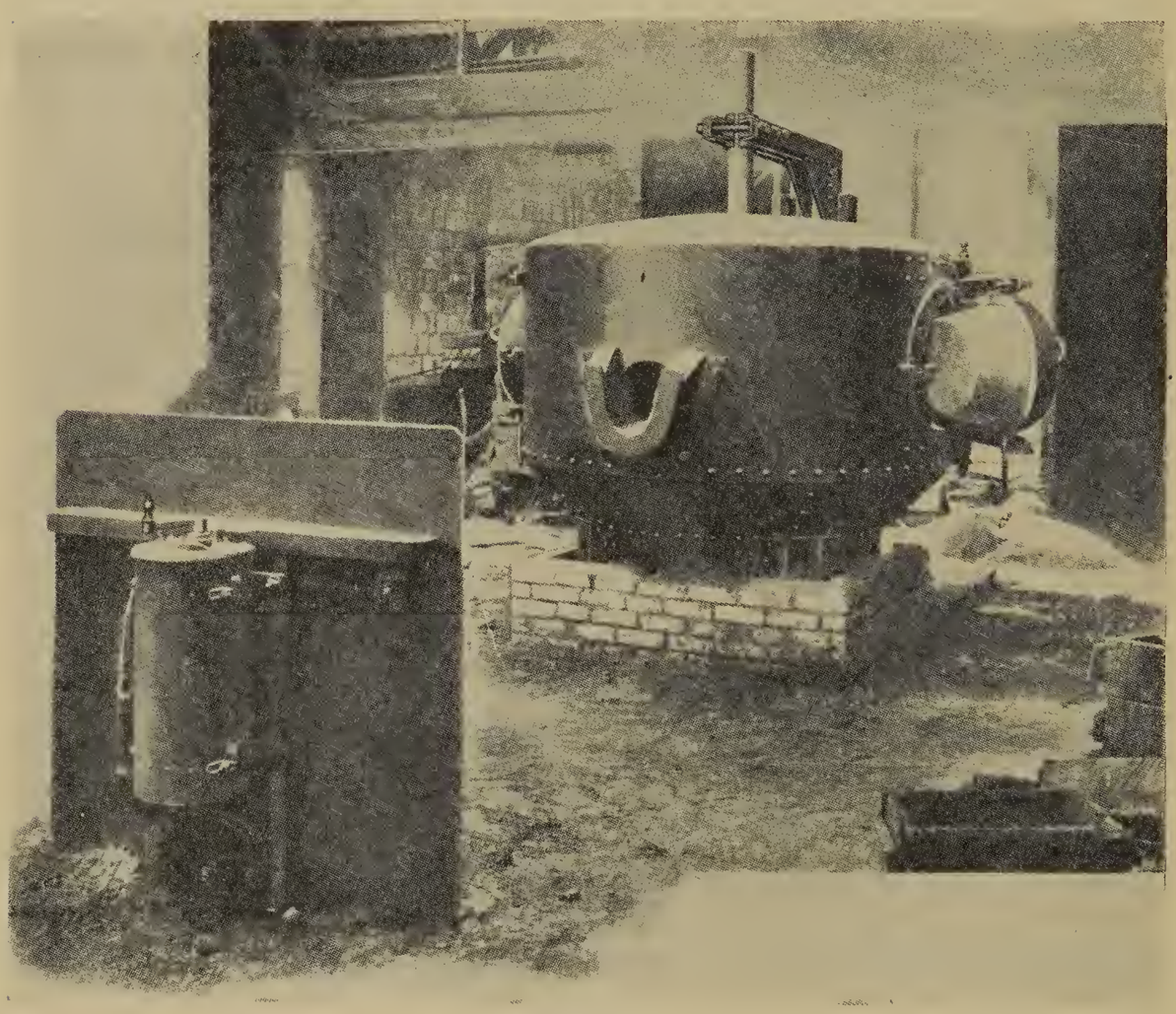

FIG. 2.

Snyder Furnace, Showing Plug Type of Furnace Door.

The principal unavoidable heat loss in an electric furnace is through the electrodes. Just as a copper wire conducts electricity better than air, so a carbon electrode conducts heat much better than would the air in an empty electrode hole. With the three electrodes used with most furnaces of earlier design, and with the three electrodes of the same size as the single electrode, the heat loss would obviously be three times as great as in the single-electrode furnace. Actually, the ratio is much higher, due to the economic necessity of using amorphous carbon electrodes in

three-electrode furnace. As used in the best actual practice the cross-sectional area to the three carbon electrodes of a three-electrode furnace is about fifteen times the cross-section of the one graphite electrode of the single-electrode furnace. Carbon at these temperatures has about half the heat conductivity of graphite,[2] so that the heat lost through the three electrodes is about seven and one-half times the heat lost through the one electrode. However, with the single-electrode furnace a contact is also required to connect the charge with the circuit. This contact loses some heat, hence the net result is that the heat loss due to the introduction of the current in a well designed three-electrode furnace is about five times the heat loss in a one-electrode furnace.

A substantial loss of heat with the older designs is due to furnace delays. If the pouring gang are not ready to take the heat the moment it is finished, the high radiation losses of the furnace of older design keep on and are frequently augmented by the melter allowing the temperature of the bath to keep on going up. The furnaces from which the records given here were taken are inherently designed to regulate automatically for maximum temperature. As the temperature reaches that for which the furnaces were designed, the electric input is just sufficient to keep up the radiation. This reduces largely the loss of heat due to furnace delays. In addition, it prevents largely the overheating of refractories. This regulation for maximum temperature is secured without auxiliary apparatus of any kind. In each case it is an inherent characteristic of the furnace design.

The low labor cost with these furnaces is due primarily to the simplicity of the mechanical and electrical construction. The smaller of the furnaces is handled entirely by a single man, except when charging, when three helpers are used to shorten the charging time. Due to the fact that the furnace is entirely and inherently self-regulating, this single melter, for something over half his time, has nothing to do at the furnace. On occasions each of these furnaces has been left for an hour at a time without attendance, at work at full power. This extra time the

[2] Carl Hering: Trans. Am. Inst. Electrical Engineers, March, 1910, p. 285, gives the conductivity of graphite at 1600° C. as 2.9 watts per inch cube, of amorphous carbon 1.5 watts.

single melter uses in making ready the next roof and in shearing up scrap for easy shoveling.

The other material factor in the low labor cost per ton of these furnaces is their rapid melting ability and the consequent relatively large tonnage output per man, as shown in the labor items in the tables given, expressed per ton of steel. This output capacity is in turn due to the fact that the electric input is not wasted, but very largely goes to melting steel. This effect is cumulative, as the shorter time of heats reduces the radiation time chargeable to each ton, and so releases further energy for melting steel. This in turn reduces the labor cost per ton of output for a definite size of furnace.

In closing, it may be stated that these furnaces show a thermal efficiency not far from double that usual with furnaces of older design. The most reliable figures we can get for regular operation of furnaces of older design operating on a single shift show about 1,000 K.W.H. per ton of steel, of which only 33 percent goes into the ladle with the fluid steel and slag; our furnaces under equivalent conditions use only about 560 K.W.H. per ton of steel, the corresponding efficiency being 63 percent. This is important commercially. The slow progress of electric steel making in the first ten years of its commercial existence was due to its high costs. It could not compete with most types of fuel furnaces in cost per ton of output. Its plea for existence had to be based on quality of product. The advance in this country, where quality was relatively unimportant, was slow. These furnaces of newer design give costs that are lower than most types of fuel furnaces. The higher quality of electric steel is secured for nothing. The real competition in the past has not been between different types of electric furnaces, but between all types of electric furnaces and fuel furnaces. Now that properly designed electric furnaces can compete in cost with fuel melting on steel, their introduction in this country should be accelerated.

DISCUSSION.

F. A. Lidbury (*Communicated*): This paper contains a great deal about the reasons why certain results are attained; but it does not tell us nearly enough about what those results are. If

the intention is to make these records of use to prospective users of electric melting furnaces, complete information should be given as to (a) nature of scrap used, (b) nature of treatment, including full details of alloys, etc., added, (c) nature of steel produced, and purpose for which it is employed. "Steel castings" would be but an indefinite reply to (c); the term not only covers a wide variety of shapes, sizes and purposes, but it is elastic enough to cover a large number of "steels" of very weird nature.

While the matter does not directly arise out of this paper, it would be of much interest to the Society if Mr. Snyder could see his way at some future time to describe the interesting rectifying effects which are understood to have been found to accompany the use of such relatively high-voltage arcs under certain conditions of operation.

President L. Addicks: This is a rather unusual paper, as it appears to give an actual record of costs, and very few of our contributions carry such figures. I think it is particularly valuable on that account, and, while the work relates to a very narrow field of special steel, it seems very probable that this field may be broadened to where the tonnages may be of considerable importance.

D. A. Lyon: In looking over the paper I was impressed by the fact that it contained a great deal of valuable cost data. On the other hand, I wondered whether Mr. Snyder was keeping anything back or not. I have not had very much to do with steel, and so I am not prepared to say as to whether these costs are fairly representative or not. I find, in going from place to place, that there is such a wide difference as to what is given you in the way of cost data, that it is pretty hard to place any reliance on such data, except on the cost of power, the cost of electrodes, and so forth. You have to be quite familiar with the work which is being carried on before you can arrive at any conclusion as to costs, except as to the cost of power, refractories, and the other material used.

President L. Addicks: The cost on page 223 appears to be $3.80 per ton, with the kilowatt-hour cost of seven-tenths of a cent; and that figures out something between five hundred and six hundred kilowatt-hours per ton, against the furnace in the pre-

vious paper of 780 kilowatt hours per ton. So, if these figures are reliable, it would appear that the furnace is more economical than the one tested by Wills and Schuyler.

J. W. Beckman: I would like to have some statement as to whether there is not considerable loss in wattless currents.

Secretary J. W. Richards: The comparison of this furnace with the one tested by Messrs. Wills and Schuyler is correct The difference is due to the much superior design of the Snyder furnace. In several details, this furnace of Mr. Snyder is adapted or designed to reduce the heat losses very considerably; and I think that there is ground for believing that Mr. Snyder has attained very nearly the efficiency which he states.

Some of these details are as follows: He uses a very small graphite electrode, so small that its heat conductivity is thereby limited, as Mr. Williamson mentions, so that he obtains minimum electrode loss.

Then, the door of this furnace is a special plug type, shown in the picture on page 228. It is a very great improvement on the ordinary electric furnace door. The furnace described by Wills and Schuyler had a door about one brick thick, while the wall was eighteen inches thick, and therefore they were losing far more heat at the door than an equal area of the walls. It was, moreover, a poorly-fitting door.

I have seen an induction electric furnace in operation where the lids over the fused steel were fire-clay plates originally six inches thick, but they were worn down to one inch or two inches, and were radiating heat at a frightful rate. Such a furnace could easily consume twice as much power for a given amount of metallurgical work done as one having a heavy door such as Mr. Snyder designed. He has also lagged or jacketed his furnace with poorly conducting brick, a scientific application of low heat conductivity materials.

One thing I suggested to Mr. Snyder which he did not adopt was to paint or plate his furnace, so as to make it white on the outside. I know of one electric furnace which, by painting with white aluminium paint, had its power consumption reduced from 67 to 58 kw., for the same working temperature. That was over 10 percent saving on that small furnace, simply by painting the

outside. If Mr. Snyder's furnace could be given a Monel metal casing, such as Prof. Northrup's electric furnace, the radiated heat could be still further reduced. When we consider that in the ordinary electric furnace now used probably not more than one-half of the energy goes to melting the steel, the importance of reducing these radiation and conduction losses should be recognized.

I know of no one who recognizes them more practically than does Mr. Snyder, and he deserves much credit for his enterprise in applying scientifically the means for reducing losses from the furnace. But whether he is getting seventy-five or eighty percent efficiency or not, I believe that his electric furnace is melting steel with an efficiency equal to that of the very best, and superior to most of the electric steel furnaces now in use.

President L. Addicks: I notice that Doctor Richards is still loyal to aluminum paint, where he wants the furnaces painted white.

On page 230 the author says that the older furnaces use one thousand kilowatt-hours per ton, and now he gets it down to six hundred.

J. W. Beckman: If you examine the recent literature now published regarding these so-called "older types" they all give close to the same power consumption per ton of steel as Mr. Snyder offers.

Secretary J. W. Richards: There is an electric furnace which comes close to Mr. Snyder's in scientific design, and that is the Rennerfelt Furnace, which has been described in the Journal of the Iron and Steel Institute for 1914. For ferro-manganese they give an energy absorption of 450 kilowatt-hours per ton melted, which is not very far from what Mr. Snyder says he uses.

A. M. Williamson: Mr. Snyder's statement regarding the comparative electrode consumption in single and three-electrode furnaces is, I believe, open to some criticism. The comparison is apparently based on the consumption in the Snyder furnace as representing the single-electrode type compared with three-electrode furnaces running on carbon electrodes. There are, however, single-electrode furnaces in operation in which the electrode consumption approaches that in three-electrode furnaces, both types

of course running on the same kind of electrodes. Experience has shown that, other conditions being equal, graphite electrodes show the same relative economy when used in three-electrode furnaces as in single-electrode furnaces.

SECRETARY J. W. RICHARDS: On page 229 it is said that carbon, at the temperatures of this furnace, has about one-half the heat conductivity of graphite. These were Mr. Hering's results. But Mr. Hering's experiments were made in a way which does not apply to the majority of electrodes as used in electric steel furnaces. Even if they were correct for Mr. Hering's conditions, they certainly do not apply to the use of the electrode as Mr. Snyder uses it, through the roof of his furnace. It is likely that carbon electrodes at these temperatures, and used in this way, would have probably only one-eighth of the heat conductivity of graphite, instead of one-half. I have measured the actual heat conductivity of graphite compared with ordinary carbon at relatively low temperatures, up to one thousand degrees, and it is ten times that of the carbon. So the figures of Mr. Hering are probably not applicable to the use of an electrode in this way in the steel furnace.

A. STANSFIELD (*Communicated*): This paper is a little difficult to discuss because Mr. Snyder presents us with the results obtained by his furnace, but, no doubt for sufficient reasons, is unable at present to explain to us exactly how he obtains his results. Whoever attempts to criticize his paper is liable therefore to be guessing at random in regard to the explanation.

Taking first the results obtained in regard to costs, these refer of course to the simple melting of steel scrap without any refining operation. Figures referring to the same process have been given by Mr. C. A. Hansen in the *Transactions* of this Society.[1] Mr. Hansen quotes 900 K. W. hours as the power consumption per ton of steel, while Mr. Snyder's figure corresponds to under 600 K. W. hours. The costs for repairs and electrodes quoted by Mr. Hansen were each $2.50 per ton, while the corresponding figures given by Mr. Snyder are 60 cents for electrodes and probably a similar figures for repairs. These reductions, assuming that they really represent an improvement in the furnace and not

[1] C. A. Hansen, "Electric Steel Castings," Trans. A. E. S., Vol. xxv, 1914, p. 133.

merely a difference in the operation, are very important and well worth the consideration of those engaged in steel foundry practice.

The explanation offered by Mr. Snyder for the reduction of power cost may be summarized as follows:

1. Smaller loss of energy by electrodes.
2. Smaller loss by construction of doors, etc.
3. Smaller loss by thicker and better designed walls and roof.
4. Smaller loss by greater speed of operation, thus reducing the time during which heat is lost.

Mr. Snyder explains that his furnace is operated at a higher voltage than is usual in three-electrode furnaces, and I understand that a voltage of 220 is contemplated. The use of a high-voltage supply will undoubtedly reduce the electrode loss, because a smaller electrode will serve to supply the same amount of energy to the furnace. This change of voltage will correspondingly reduce the loss of electrode material and so effect a further economy.

I have calculated[2] that the electrode loss in the case of a Heroult furnace, operating at 100 volts and with correctly designed electrodes, would be about 5 percent of the power supplied. If. Mr. Snyder's arrangement saves one-half of this amount, the economy would not be very important. In actual practice the electrode losses might easily be much more than 5 percent on account of the electrodes being stouter than required by theory and because the furnace is not operated continuously at full load. If the Heroult furnace losses should amount to 10 percent it is quite probable that Mr. Snyder's furnace might save half of this, or 5 percent of the total power. This would represent from 30 to 50 K. W. hours per ton, and would be well worth saving.

With regard to the roof of the furnace, this is said to be considerably thicker than in most furnaces, but we are not told whether the roof is of silica brick, as is frequently the case, or of magnesite brick or similar more refractory material.

Single Electrode Furnace: The use of a single electrode has certain advantages in regard to simplicity of construction and greater durability of the furnace roof. It involves the use of

[2] Stansfield "Electric Furnace," 1914 Ed., p. 107.

a conducting hearth; that is to say a hearth containing a steel electrode, usually water cooled. Persons conversant with the operation of the large steel-making electric furnaces have condemned this type of electrode, stating that it is impossible to maintain, in good condition, the hearth of a steel furnace which is pierced by one or more rods of steel. The design of a furnace with one upper electrode is, for many reasons, superior to that with two or more electrodes entering through the roof, providing the difficulty of the conducting hearth has been overcome.

Mr. Snyder does not explain how he obtains single-phase current for operating his furnace. Electrical power in large quantities is usually available as a three-phase supply, and using it to operate a single-phase furnace would commonly result disastrously. This is a point rather of electrical engineering than of electric furnace design, but it should not be forgotten, and might materially affect the cost of the energy.

High-Voltage Arc: The earliest electric steel furnace, invented by Stassano, was of this type; maintaining between two or more carbon electrodes, an arc of 150 or 200 volts. This furnace was not very efficient, no doubt because the arc would tend to rise in the furnace and therefore to heat the roof rather than the charge. This difficulty has been overcome in a more recent furnace invented by Mr. Rennerfelt of Stockholm,[3] who uses three electrodes and a two-phase arc. This arrangement has the effect of projecting the arc downwards from the electrodes onto the metal, although the metal is not part of the conducting system, and the furnace can be operated empty.

In Mr. Snyder's furnace the arc necessarily travels between the electrode and the metal charge, and therefore the heat will pass into the metal somewhat more rapidly than towards the roof of the furnace. One important advantage of a high-voltage supply will be that during the melting of the metal scrap in the furnace the arc will be less likely to break than in the case of a low-voltage furnace, and there will therefore be no need of frequent regulation of the electrodes. Mr. Snyder points out that a high-voltage arc has a less intensity of radiation and therefore a lower general temperature than a low-voltage arc, so that the

[3] A. Sahlin, "The Use of Liquid Ferro-Manganese in the Steel Process" (Iron and Steel Inst. (1914), 90, 213).

furnace is heated more uniformly than by a single arc of the low-voltage type. The whole efficiency of this style of heating must depend, however, on the possibility of maintaining refractory walls and roof which can stand the heat radiated from the arc without melting, and also without conveying away too large a proportion of the heat. The furnace just referred to, invented by Mr. Rennerfelt, aims at obtaining these results. It is built in a horizontal steel drum and the refractory lining consists of a complete cylinder of magnesite brick forming both the roof and the hearth. This magnesite brick, being strongly arched, stands up well for the roof and is backed by asbestos and other non-conducting material which serves to retain the heat.

Self-Regulating Furnace: Mr. Snyder states that the furnace is practically self-regulating; that once started it draws a steady load without any need of regulating of the electrodes, and further that when the furnace has reached its working temperature the energy input decreases automatically so as to avoid an undue rise of temperature. In operating any high-voltage arc furnace it appears to be necessary to have some resistance or reactance in series with the arc, which would otherwise be unstable. Mr. Rennerfelt finds it necessary to use a steadying resistance in series with each of his arcs, to obtain a steady load, although in some works, where the steadiness of load is less important, this resistance has been omitted. In ordinary arc lighting the regulation of the arc is effected by having transformers that supply a constant current rather than a constant voltage, and it is quite reasonable to suppose that for these high-voltage arc furnaces easier regulation could be obtained by the use of some regulating transformer. As the temperature of the furnace rises the resistance of the arc will fall, and if the voltage of the supply were constant the power admitted to the furnace would consequently increase, whereas if the current were constant the power would decrease. It may be, therefore, that Mr. Snyder's regulation is based on the use of some regulating transformer in the substation referred to in his table of costs, and this would certainly seem a desirable method of obtaining the desired regulation in a simple manner.

Mr. Snyder states, however, that "This regulating for maximum temperature is secured without auxiliary apparatus of any

kind" and is "an inherent characteristic of the furnace design." In view of this statement it seems more probable that he utilizes the reactance that is inherent in a single electrode furnace, where the path of the current passes through the steel casing of the furnace. Assuming that this reactance prevents any considerable increase of the current beyond the normal amount, the power would remain fairly constant during regular operation, and would actually fall owing to the decreasing resistance of the arc, as the temperature of the furnace increases beyond a certain amount. No figure is given for the power factor of the furnace, and we are therefore unable to judge whether this is so low as to react unfavorably on the conditions of the electrical supply.

A paper read before the Pittsburgh Section of the American Electrochemical Society, April 14, 1915, and called up for Discussion at the Twenty-eighth General Meeting of the Society, in San Francisco, September 16, 1915, President Addicks in the Chair.

ELECTRIC FURNACE MELTING OF FERRO-ALLOYS

By R. S. Wile.[1]

Among the many things that this war has brought about is the high price of metals. This is due to several causes: large consumption abroad, inability to receive shipments, and embargoes by foreign countries. Among the metals whose prices have soared are the ferro-alloys of manganese, silicon, chromium, etc., the chief source of supply of which is abroad.

With these alloys reaching high figures, and with bad business conditions in this country, it becomes necessary to use less alloy or to raise the price of steel. As neither of these is advisable under existing conditions, more economical methods of using them must be sought, and for that purpose we are exploiting our electric furnaces.

One way of doing this is to melt the ferro-alloy before adding it to the ladle, thereby saving a large part of the metal usually lost, and also improving the steel by avoiding segregation because of thorough distribution. This also means easier working of the steel.

The work we have been doing in ferro-alloys is not confined to open hearth practice alone, but in melting the alloys for other practices as well.

Mr. Skinner, of the Westinghouse Company, was at Niagara Falls last October when I was demonstrating a furnace for the smelting of tin dross, and he suggested that I get in touch with him upon my return, which I did. We sent a small furnace out to their plant for demonstrating and it was used for several purposes, among them being the melting of nickel-iron for casting grid resistances. It is necessary to keep a high graphite content in the iron to maintain its toughness, and to have the specific

[1] President, Wile Electric Furnace Company, Pittsburgh, Pa.

resistance of one heat similar to another in order to do away with the tedious testing and sorting of the heats, so that they will correspond. These requirements are rendered more difficult by the high temperature necessary to pour the very thin castings demanded. Great care must be exercised to prevent the change from iron to steel at this temperature, for while the iron is very tough the steel is very brittle, hence it can readily be seen that there are some requirements which would prevent the use of some kinds of furnaces for melting this material. The tests in the small furnace warranted their installing a larger one of 500 lb. capacity per heat. A grid cast from this furnace is shown.

The largest use for our furnace is, however, for open hearth practice.

A condition which occurs in most steel plants is a variable supply of power due to the electrical equipment being used intermittently. A furnace of the slag resistance type can be used to good advantage for melting ferro-alloys during these periods of idleness, as it can be retarded or advanced at will without serious damage other than delaying the melting of the alloy, but as the composition of the alloy does not change during melting it does not affect the material in the least to keep it in the furnace longer, the only inconvenience being in the case of several furnaces being ready to tap in quick succession, in which event it is necessary to draw upon the power supply. The advantage of melting the alloys is apparent in almost every instance, but more particularly where large additions must be added to fifty-ton ladles, causing a decrease in the temperature of the steel, often rendering it necessary to tap the ladle before the additions are thoroughly distributed. Not only does this make working difficult but it makes it necessary to stock the part not conforming to specifications. The handling of this steel and the inconvenience caused would greatly offset the cost of the electric furnace and its operation, without figuring in the saving of metal, which must be taken into account at any time, but more particularly now that the cost has advanced.

This country has never given much attention to the manufacture of special steels, most of these having come from abroad, but now that the supply has stopped more attention is being given it here, but it finds us largely unprepared. Very few mills are

so equipped that they could add 3,000 lbs. of ferro-chromium to a 50-ton heat of steel. Even though they could handle it, there would be no certainty of the composition when it was tapped, and it is for these cases mentioned that our furnaces have found application.

I will give a brief description of the furnace before going into results, in order that its operation may be clearly understood. The furnace is of the three-phase type, one bottom and two top electrodes. The spacing of the electrodes is such that they compose, as nearly as possible, an equilateral triangle. To start, the two top electrodes are lowered to the floor of the furnace, some granular graphite or plumbago is sprinkled in and when this glows the slag-making materials are added. These vary with the material, but window glass is used for most purposes, as it is neutral to most of the metals to be melted. As this melts the electrodes are raised until the proper height is reached, and the alloy is then charged into the furnace and is melted beneath the slag from the heat of the bath and not from the direct heat, as in the case of the arc furnace. No auxiliary mechanism is used, the current coming direct from the transformer to the furnace, the heat being regulated by the depth of the electrodes in the slag. When the metal is melted it is either poured into an auxiliary ladle and thence into the steel ladle, or the entire electric furnace is picked up by the auxiliary hoist of the crane and the furnace poured as if it were a ladle. The slag stays in the furnace to be ready for the next heat. It retains its molten condition for a considerable length of time, which enables the power to be quickly picked up again. If the furnace is used as a ladle it is set down by the auxiliary before the big ladle is poured, and is either picked up by another crane and put into place or kept where it is until the ladle is poured and then replaced. This latter course, however, dissipates a good deal of valuable time and is not conducive to the highest efficiency of the furnace.

It may be questioned by many as to the advantages derived from introducing the alloy in a molten condition, other than those of distribution, etc. I mean the saving of metal effected. The percentage of saving varies with the amount of manganese added to the steel. As is well known, a great part of the manganese

added to both open-hearth and particularly Bessemer steel is lost in freeing the steel of oxides, and the amount of manganese oxidized is less with a high carbon than with a low carbon steel—it decreases with the amount added. Thus, if 1.00 percent manganese be added to the bath, 0.60 will be found in the steel (loss 0.40); if 0.60 percent be added the steel will retain 0.40 (loss 0.20). The loss in one case is 40 percent and the other 30, and there is no assurance that all parts of the steel will show 0.60 percent or 0.40, as the case may be. The function of the manganese then is two-fold, one to reduce the oxides, but mainly to strengthen the steel, but tests and practice have shown that by adding the manganese while molten the losses shown above do not occur so heavily, and that a larger percentage of the manganese is retained in the steel. The saving is often as much as 35 percent of the manganese used.

The following extracts from an article by Felix Schröder, of Livet, France, giving the results of melting over 1,000 tons of ferro-manganese are interesting and give some idea of the cost in an arc furnace. The costs of doing this in the resistance furnace are somewhat less, as later figures will show.

The results obtained with one furnace of the Keller system at the Burbacherhütte in Saarbrücken are described. It was adopted there after previous tests at the works of Keller-Leleux Company in Livet had shown the possibility of melting 80 percent ferro-manganese in the electric furnace without any losses of manganese. The furnace was designed for the manufacture of steel and was run alternately on steel and ferro-manganese during the last nine months. The use of molten ferro-manganese was begun at once on a large scale. More than 1,000 tons of ferro-manganese have been remelted in the electric furnace, to be used as molten addition to all basic converter metal, in the ladle, for several months.

The continuous operation of the converter plant during the six weekdays required an uninterrupted running of the electric furnace in order to have hot ferro-manganese ready whenever needed. On Sunday the metal usually remained in the furnace and was maintained fluid by the electric current, the consumption of electric current for this purpose being "very low." When no electric power was available the furnace was emptied and

restarted on Sunday night. During the week the furnace was never emptied. Small repairs were done on Sunday, the hot metal meanwhile being poured into a ladle.

The longest period during which the furnace was used for melting ferro-manganese was three months. During this time the roof of acid brick, which had already been used before during a period of steel refining, was neither repaired nor renewed. The dolomite lining was not renewed, and only a few small repairs were made from time to time. After these three months of ferro-manganese melting the furnace was started to run on steel again, and the lining was still in fair condition. The roof and lining of the furnace when used for melting ferro-manganese, therefore, last at least three months, and the author claims that a lining of magnesite would stand from six to nine months in continuous operation. The inclined lower lining between door and hearth and also the lining of the hearth itself were not changed for nine months, requiring only a few repairs.

From the results obtained at the Burbacherhütte, the following conclusions may be drawn:

1. The remelting of ferro-manganese in the furnace occurs without any losses of manganese by volatilization.

For example, 10 average samples of solid ferro-manganese had the following analysis: 80.29 percent Mn.

Thirty-seven successive samples of molten ferro-manganese taken from the electric furnace had the following analysis: 80.22 percent Mn.

The remelting, therefore, causes practically no loss of manganese. There is no smoke nuisance at the furnace.

2. The net saving due to the use of molten ferro-manganese amounts to 35 percent of the amount of solid ferro-manganese which would be necessary for the production of steel of the same quality and under the same conditions of operation. Another saving results from the fact that all the small pieces and "fines" of ferro-manganese, which are usually lost in ordinary practice, can be used up.

In this comparison it is assumed that the same amount of manganese shall be in the finished steel as in usual practice. As a matter of fact, however, it is possible, if the addition of ferro-manganese is made in molten form, to reduce slightly the man-

ganese content in the finished steel without affecting the rolling quality.

3. Costs of melting based upon a price of 0.5 cent per kw-hour were approximately $5 per ton of ferro-manganese, including electric power consumption, electrode consumption, wages, linings, and repairs. These are not the costs of special experiments, but a monthly average, and therefore include costs of heating and starting the furnace, delays, interruptions due to electrode changes, Sunday work, etc., or, briefly, all the expenses of using the process in a commercial basic-converter plant.

Assuming that the melting-cost per ton of ferro-manganese is $5, the price of one ton of ferro-manganese $40 only (abroad), and that 5 kg. of ferro-manganese are to be used per ton of steel, we obtain the results given in Table I.

TABLE I.

Yearly production of steel, tons	Ferro-manganese remelted, tons	Total Melting Cost, dollars	Saving of Ferromang. (if 1 kg. of Ferromang. is saved per ton of steel) tons	Price of Ferro-manganese saved, dollars	Saving of Ferromang. (if 2 kg. of Ferromang. is saved per ton of steel) tons	Price of Ferro-manganese saved, dollars
100,000	500	2,500	100	4,000	200	8,000
200,000	1,000	5,000	200	8,000	400	16,000
300,000	1,500	7,500	300	12,000	600	24,000
400,000	2,000	10,000	400	16,000	800	32,000
500,000	2,500	12,500	500	20,000	1,000	40,000
600,000	3,000	15,000	600	24,000	1,200	48,000
800,000	4,000	20,000	800	32,000	1,600	64,000

It may be said that, on account of the smaller ferro-manganese consumption, the weight of steel produced is also smaller. The slag is also less. The useful phosphorus in the slag increases and there is no reduction of phosphorus back into the metal. All these facts have a very small influence on the final results.

The above consumption of 5 kg. ferro-manganese per ton of steel is an assumed figure; it will in reality vary according to the quality of steel produced at different plants, therefore the calculation should be considered only as an example. It shows, however, that in no case do melting costs exceed the saving in ferro-manganese, even if only 1 kg. of ferro-manganese per ton of steel should be saved. But the situation is improved considerably if 2 kg. or more of ferro-manganese can be saved.

Besides this, the use of ferro-manganese offers many other

advantages which should not be overlooked. The desired quality of the steel is far more easily obtained than is possible with the use of solid ferro-manganese. All of the molten alloy is completely absorbed by the hot metal. With some experience in estimating the manganese contained in a sample of converter metal taken after the blow, it becomes easy to determine accurately the amount of ferro-manganese to be added. This is of great value for high-carbon steels.

Using solid ferro-manganese on cold heats in the converter, one always runs the risk of it not being absorbed in the bath, but using molten additions, the distribution of molten ferro-manganese in the ladle is uniform, the deoxidation quick and more effective, and rephosphorization impossible.

Not only is the quality of the steel improved, but the capacity of the converter plant can also be increased, since the time required for the resting of the metal to permit the ferro-manganese to dissolve is saved. The gain per heat is always a few minutes, which amounts to something when running full capacity.

There is no reason why this process should not be successfully employed in open-hearth practice.

We have carried out extensive tests to prove that there is no change in the alloy while melting, and to show the carbon electrode and power consumption, as well as the cost of linings, in our furnace, and we have come to the following conclusions, using 80 percent ferro-manganese as a basis: The average power consumption is nearly 800 K. W. H. per ton; the carbon electrode consumption is never over 12 pounds per ton and rarely that; the lining cost is between 10 and 25 cents per ton, depending upon the rapidity of melting. This means that the cost, with power at 0.5 cent per kilowatt hour and carbon electrodes at 4 cents per lb. will be between $4.50 and $4.75 per ton, exclusive of labor, which is incidental to the plant anyhow. This will add to the cost of the average steel between 3 and 10 cents per ton—a very small amount, which is easily compensated by the reduced handling. Another point of saving is in closer calculations of the manganese, in this manner, as stated before. If the specification calls for 1 to 1.25 manganese the proper amount can be melted to yield the 1 percent in the steel, thereby saving the 0.25 percent.

Most of these remarks have been confined to ferro-manganese, but the saving in ferro-chromium is easily greater, as this alloy is now charged into the steel while in the open hearth, where the loss is greatly increased. Without an electric furnace it is necessary to do this owing to the high melting point of the alloy and the impossibility of its becoming melted by the time of pouring the ladle. It is truly wonderful to contemplate the saving possible by pre-melting this alloy.

I have taken up a great deal of time in the matter of the alloys, and I will pass quickly over the smelting of Bolivian tin ores and concentrates. As you doubtless know, this has never been done on a commercial scale in this country. In the countries where it was smelted it was done in reverberatories, and the slags which were basic in character were re-treated in blast furnaces. These slags carried from 15 to 20 percent of tin before re-treating, and from 2 to 3 percent after re-treating. The tin ran about 95 to 96 percent pure. We were required to smelt a lot of these concentrates, which we did, using an acid slag with a loss of 1.89 percent tin in the slag or 0.5 percent of the tin content, recovering tin which ran 98.75 percent pure, without any refining and with an expenditure of less than 450 kilowatt hours per ton of concentrates. A smelter is now under way for handling these concentrates in this city. At present the ores are over-concentrated, and it is necessary for us to add silica and other fluxes to them, these fluxes having been originally in the ore. The analysis of the concentrates treated was as follows:

Tin	66.96
Silica	5.24
Iron	0.92
Sulphur	1.14

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, at a Joint Session with the American Institute of Mining Engineers, September 17, 1915; President L. Addicks of the A. E. S. in the Chair.

THE THERMAL INSULATION OF HIGH-TEMPERATURE EQUIPMENT

By P. A. Boeck.*

The thermal insulation of high-temperature equipment for industrial purposes is a subject that has not received from engineers and designers the attention its importance deserves. This may be attributed to a number of causes: In the first place, heat flow is a rather difficult factor to measure under the working conditions of an industrial furnace, and until the comparatively recent introduction into certain operations of the heat balance sheet, with a systematic attempt to account for the discrepancies in the totals, the various causes of heat losses and the reasons for their existence were not brought to light. Moreover, such rapid advancement and radical changes in the design of equipment, especially in metallurgical lines, have occurred that practice has apparently outdistanced the theory of design. In the modern tendency toward greatly increased size of units, effort has seemingly been made to utilize the heat of fuel gases without proper attention having been paid to conserving heat energy and confining it strictly to the points of maximum activity.

The systematic study of the thermal properties of structural materials, which is being carried out by various government bureaus and also by a number of technical societies, is forming the basis for more intelligent and consistent work in the economically important subject of prevention of fuel waste.

Advantages of Insulation

It is not necessary in this practical and utilitarian age to enlarge upon the need of prevention of heat losses, but attention may advantageously be called to the other benefits derived simultaneously with the saving in fuel and the increase in thermal capacity of furnaces when properly insulated.

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In most industrial furnaces—which are here spoken of in the broadest sense, as indicating general high-temperature equipment for any purpose and heated in any manner—the operations are generally carried on through a temperature range which has been found by practice to give the most effective results. If, in preventing the heat being dissipated from the outside of the furnace, the temperature throughout the furnace is made more uniform, the zone of reaction is manifestly greatly increased without additional fuel consumption. Furthermore, overheating at the source of heat, in the effort to bring as much of the furnace as possible into the zone of reaction, is materially reduced by preventing the loss of heat through the furnace walls. This has the ultimate effect of lowering the temperature at the source of heat and greatly increasing the life of the refractories—usually an important factor in high-temperature work. It is evident, too, that in furnaces which are surrounded by metallic casings or other equipment susceptible to the action of high temperatures, the deterioration and damage caused by overheating may readily amount to many times the cost of installing the proper protecting insulation. The humanitarian will also see the advantages gained by the protection of workmen from the unhealthy and unsanitary conditions brought about by being compelled to labor under overheated conditions.

The importance of thermal efficiency of all manner of high-temperature equipment is now being more generally recognized and is receiving much attention.

Heat Flow

Without going into a detailed consideration of the general laws governing the flow of heat, it would be well to call attention briefly to the following facts regarding heat flow, which will be illustrated by reference to the steam boiler as a well-known example:

The U. S. Bureau of Mines has treated[1] this subject in a remarkably clear and concise manner in Bulletin No. 18, to which reference should be had by those desiring to refresh their memories as to the principles of heat radiation, convection and conduction.

[1] Kreisinger, Henry, and Ray, Walter T.: The Transmission of Heat into Steam Boilers, *Bulletin No.* 18, *U. S. Bureau of Mines* (1912).

The energy in the form of heat which eventually finds its way into the water in a boiler, for example, is, of course, subsequently available in other forms. That portion, however, which is transferred to the walls of the furnace setting by any of the three methods mentioned, is conducted through the setting, if means are not provided to prevent, and is lost by radiation or convection from the outer surface of the setting. It is the heat lost in this manner, and methods for its prevention, that will be especially considered in this discussion.

Rate of Heat Flow

The rate of transfer of heat under various conditions, by both conduction and radiation, shows the relative importance of these two methods in influencing heat losses. The amount of heat conducted through a unit area from one part of the body to another is proportional to the difference in temperature of the two parts; directly proportional to the thermal conductivity of the body through which the heat passes and inversely proportional to the distance between the two parts of the body. In other words, the conduction of heat through a solid body from one plane to another is a direct function of the conductivity of the body and the difference in temperature of the two planes and an indirect function of their distance apart.[2] This is identical with Ohm's law for transfer of electrical energy.

The heat transferred from one body to another by radiation is proportional to the difference of the fourth powers of the absolute temperatures of the two bodies. While this is strictly true only of the ideal "black bodies," the variation is so small that for all practical purposes this relation holds good in ordinary procedure.[3]

Hollow Wall Construction

This relation indicates the reason why, in low-temperature work, such as refrigeration, etc., a hollow wall space is an effective insulator, whereas, in high-temperature operations, the loss of heat by radiation through a hollow wall space is so great that its insulating effect is less than if this wall space were filled with material of rather high thermal conductivity. This has been

[2] Ray, Walter T., and Kreisinger, Henry: The Flow of Heat through Furnace Walls, *Bulletin No. 8, U. S. Bureau of Mines* (1912).

[3] Gurney, Harold P.: Heat Radiation, *Journal of Industrial and Engineering Chemistry,* vol. iii, No. 11, p. 807 (Nov., 1911).

brought out by Ray and Kreisinger, who again demonstrate that the hollow-wall-space type of wall construction is much less effective as a means for preventing the loss of heat than a solid wall of any ordinary construction material of equal thickness. This is especially true if the air space in the hollow wall is near the furnace side and becomes highly heated. This is entirely contradictory to the general belief that, since air is a poor conductor of heat, air spaces built into the walls of a furnace will greatly reduce heat loss by radiation. While the heat does travel very slowly through the air by conduction, it leaps over the air space readily, by radiation, because the quantity of heat which passes across the hollow space is a function of the fourth power of the absolute temperatures of the surfaces inclosing it, which loss is enormously increased by rise in temperature.

Furnace Walls

In general, in high-temperature furnace construction, there are two separate and distinct factors which must be considered to produce an effective wall. The first of these is to provide a material having the ability to resist the action of high temperatures, sufficient mechanical strength, and, possibly, the property of resisting corrosive slags, gases, etc., without spalling or being eroded. Secondly, to prevent the excessive loss of heat due to conduction from the interior of the furnace to the outside, where it is lost. It is rare that a good refractory material is a good insulator; usually it is necessary to augment or back up the refractory with some material having a much lower heat-conducting capacity. As a general rule, light porous substances are good thermal insulators; and in a great majority of cases this depends upon their entrapped voids, their apparent density being an excellent criterion of their conducting ability.

Requirements of Insulators

The requirements of the insulating backing for the more refractory lining are rather severe; an ideal insulator would have the following properties: It should be extremely high in insulating value, and sufficiently refractory so that no fusing or excessive shrinkage would take place in that portion which is in direct contact with the highly heated refractory wall. It should not be decomposed or change greatly in volume at that tem-

perature, and it should, furthermore, be of light weight, unaffected by moisture, of convenient form, readily applied by unskilled labor, and low in cost. It should be of such composition as not to react upon or attack either the refractory material or the metal shell of the container, even in the presence of moisture; *i.e.,* it should contain no free acid radicals, and should not be broken or caused to settle by vibration or heat. It should not have high expansion and it should be sufficiently elastic to take up strains between the lining and the shell produced by temperature changes. While this is a rather formidable array of requirements, there are products upon the market which fulfill practically all of them.

Such materials as are being commonly applied to steam-temperature insulation, of which magnesia and asbestos are best known, are, of course, eliminated from consideration in the great majority of cases mentioned here. The lack of more extended practice in high-temperature insulation must be attributed to the fact that effective high-temperature nonconductors have not been generally available.

Amount of Insulation.

When the kind of refractory material that is best suited to the furnace has been determined, the next most important item is the thickness of the walls and the nature of the insulating material most suitable, and it is necessary to determine the degree of insulation which will produce the most effective results. Hering has pointed out that, in order to effect a perfect insulation, the furnace should be surrounded with an insulating material that would maintain the same temperature at any point as that of any adjacent point of the lining; in other words, that there should be a uniform amount of heat loss throughout the lining.[4]

In attempting to obtain perfect insulation, it is entirely possible to over-insulate, causing serious damage to the refractories in the high-temperature zones of the furnace. To maintain the inner walls, it may be necessary to permit a considerable flow of heat through the wall, with a corresponding decrease in the temperature of the refractories at the heated point, in order to prevent their destruction. It would be manifestly impracticable to insulate the roof of an electric steel furnace or open-hearth fur-

[4] Hering, C.: Thermal Insulation of Furnace Walls, *Metallurgical and Chemical Engineering,* vol. x, No. 2, p. 97 (Feb., 1912).

nace, for instance, with a heavy layer of insulating material, because the cost of the refractory lining which would be destroyed would be considerably greater than the cost of the heat which would otherwise be lost.[5]

In electric-furnace practice, where extremely high temperatures are encountered and where effective insulation is necessary because of the relatively high cost of current, the question of insulation, or rather over-insulation, has been given more attention than in other lines. F. T. Snyder[6] has presented a detailed study of the nature and amount of insulation which is permissible under various conditions and presents many valuable data which might with advantage be applied to other industries.

The necessity for effective insulation in stoves and other metallurgical equipment has been brought out strongly by Walther Mathesius, in a paper on High Blast Heats in Mesaba Practice.[7]

In discussing the thermal efficiency of the modern hot-blast stove and probable future methods of improvement, A. E. Maccoun, in a recent paper[8] before the American Iron and Steel Institute, points out the advantages of effective insulation and the necessity for thermal insulation to increase the efficiency of the stoves.

The requirements of an ideal insulator have been outlined, and, in order to show the various methods of application which have been worked out (some of which have been in use abroad or in this country for some time), it will be well to select the insulator which apparently most nearly meets the requirements and use this as an example of methods of construction. In the applications shown, attempt was made to cover as wide a field of use as possible, to show the scope of possible applications.

Insulation.

The insulator used, known as celite, on account of its extremely cellular nature, is a mineral product of a highly siliceous composition and of very light weight, which occurs on the Pacific

[5] Lyon, D. A., Keeney, R. M., and Cullen, J. F.: The Electric Furnace in Metallurgical Work, *Bulletin No. 77, U. S. Bureau of Mines* (1914).

[6] The Flow of Heat through Furnace Walls, *Transactions of the American Electrochemical Society,* vol. xviii, p. 235 (1910).

[7] *Bulletin American Inst. Mining Engineers,* Mar., 1915, pp. 539 to 555.

[8] Blast Furnace Advancement, *Transactions of the American Iron and Steel Institute* (1915).

Coast[9] in an exceptionally pure state. It is composed of numerous hollow cells, and weighs, in its natural rock form, air dried, from 25 to 30 lb. per cubic foot (400 to 480 g. per cub. dm.). When this material is ground properly, so as not to destroy its cell structure, Sil-O-Cel powder is produced, which weighs but 8 lb. to the cubic foot (128 g. per cub. dm.) and has a thermal insulating power about equal to that of cork, or from 10 to 12

Fig. 1. Typical Wall Construction, showing Insulating Brick Laid in Wall.

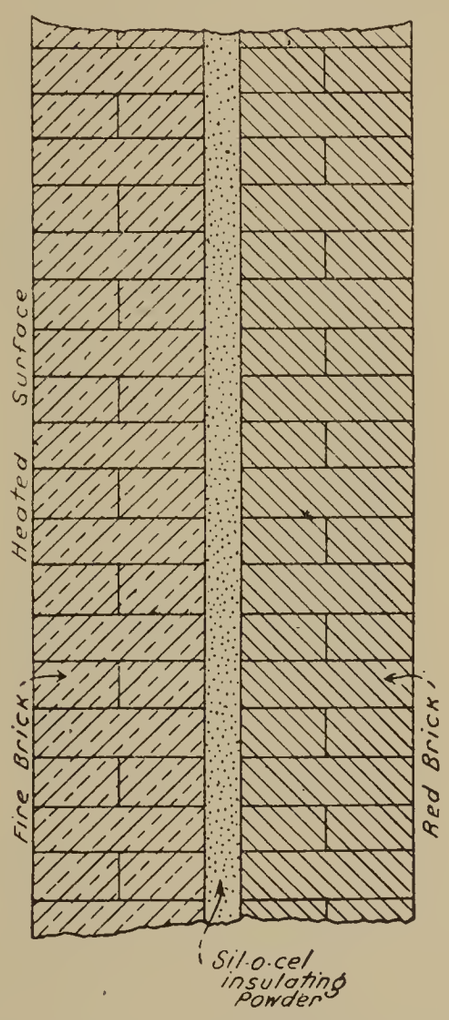

Fig. 2. Typical Wall Construction, showing Insulating Powder in Hollow Wall.

times the insulating power of ordinary firebrick. In other words, a layer of this material is the equivalent in insulating value of from 10 to 12 times the thickness of firebrick. Being almost pure silica, its melting point is high, 2,930° F. (1,610° C.), as reported by the Bureau of Standards, and it can be subjected to high temperatures without fear of alteration. It has been found advisable,

[9] Deposits worked by the Kieselguhr Co. of America, New York, Chicago, San Francisco, and Los Angeles.

however, not to use celite as a refractory at extremely high temperatures without some direct protection. This is readily accomplished by using it as a backing material for more refractory and highly conducting bodies. Owing to its remarkable nonconducting properties, the accumulation of heat on its face is so great, owing to the fact that the surface is not cooled by conduction, that a "flash" of flame or gases might easily exceed the melting point of silica and cause failure. If it is protected, how-

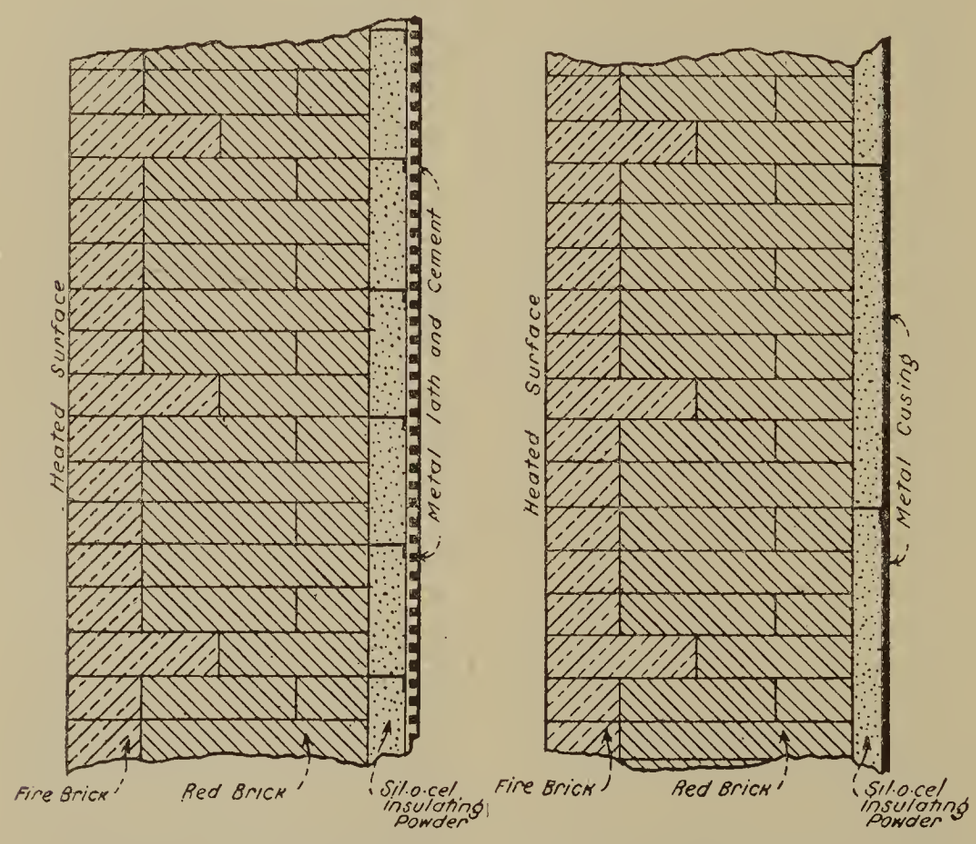

Fig. 3. Typical Wall Construction, showing Insulating Powder Supported by Metal Lath, Cement Finish.

ever, only modified and uniform temperatures are encountered, which are maintained without risk or damage.

It is possible further to prepare bricks and blocks of various sizes and shapes by sawing the natural material by means of gang saws. Standard 9-in. (22.5 cm.) straight Sil-O-Cel brick made from natural celite weigh from 1½ to 2 lb. (0.7 to 0.9 kg.) each and are equivalent in insulating value to many times their thickness of ordinary firebrick. In crushing strength, these brick withstand over 400 lb. per square inch (30 kg. per sq. cm.) and are sufficiently strong to stand transportation and handling.

The high insulating value of Sil-O-Cel bricks can be shown by applying the heat of a blast or torch upon their surface for hours, the unheated surface remaining cool enough to permit of handling. Powdered Sil-O-Cel can be tested in the same way by packing it into a shallow box of convenient size.

The cost of these insulating bricks is but little more than that of firebrick, and of the powder about one-third as much, so that the first cost of this insulation is comparatively low. In fact, instances are on record where the entire cost of insulation has been saved in fuel in the first few weeks of operation.

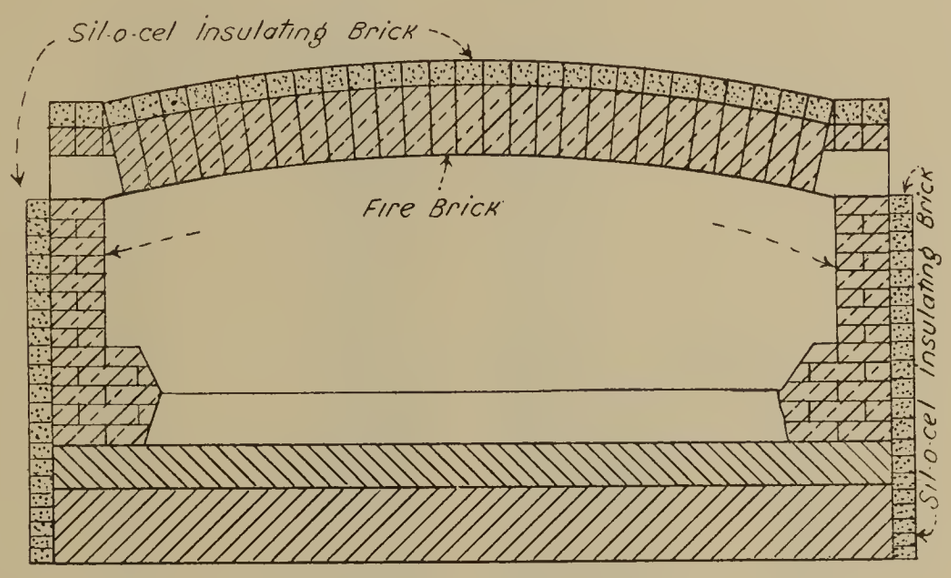

FIG. 4. Reverberatory Furnace Roof Covered with Insulating Brick.

Typical Wall Insulation.

Because of the variation in form in which Sil-O-Cel products are supplied—that of brick, blocks of various shapes, in powdered form and as a plastic cement—this material is adaptable to almost any form of thermal insulation, as will be shown in the following typical examples:

General Types

In general, there are four forms of construction for high-temperature insulation which can be adapted to almost any character of equipment.

Fig. 1 indicates the usual method of using Sil-O-Cel brick interlaid between a course of firebrick and red brick for the prevention of heat leakage through walls. This form of construc-

tion is largely used in boiler settings, bakers' ovens, reverberatory-furnace walls and roofs, etc., and is generally applicable where a strong, solid, nonconducting wall is desired.

Fig. 2 indicates one of the methods of construction of an insulating wall in which an otherwise hollow space is filled with

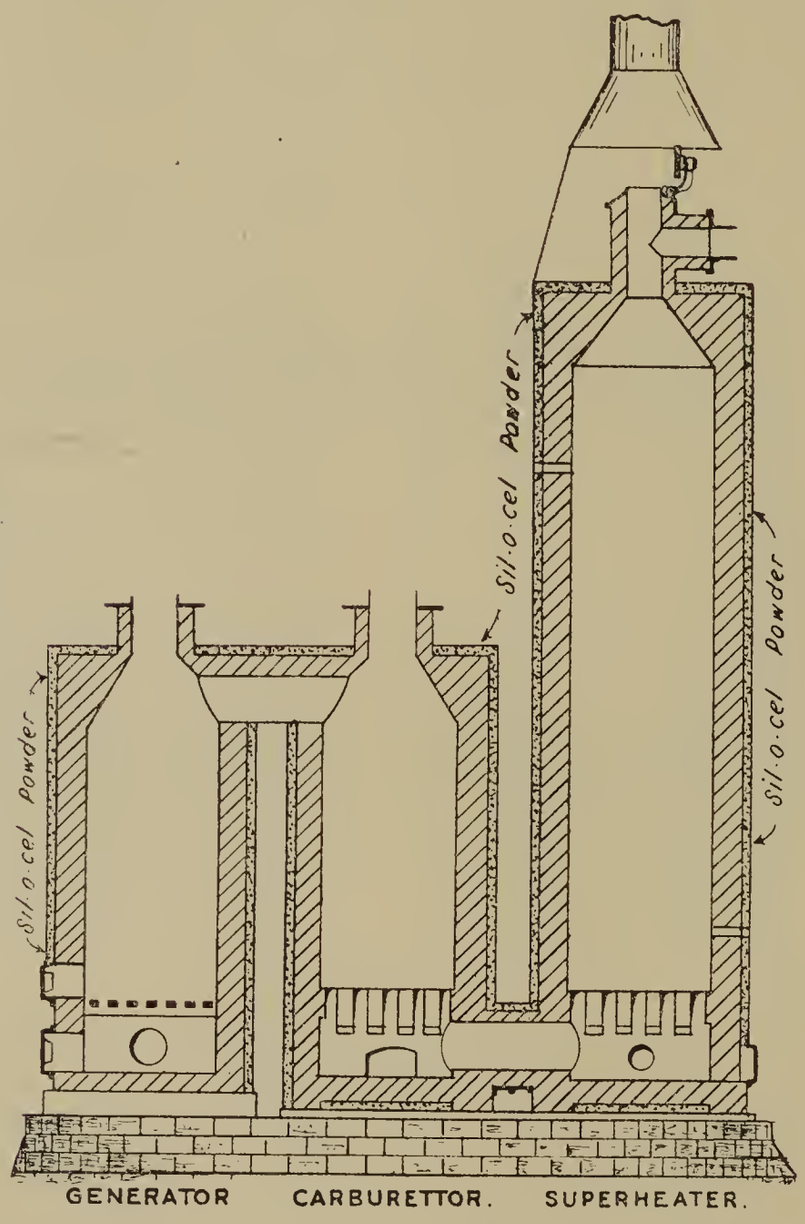

Fig. 5. Gas-Generator Set Insulated by Means of Powdered Sil-O-Cel.

insulating powder. From 2 to 4 in. are usually sufficient. The powder is packed slightly to a density of approximately 12 lb. to the cubic foot, at which point it attains its maximum insulating value and is not subject to settling or contraction due to either vibration or heat. Where this form of construction has been in severe service in high-temperature furnaces for a period of years no contraction or settling has taken place.

Fig. 3 indicates the method of insulating brick walls which are already in place. This form of insulation can be applied to old construction as well as new. In this method, expanded metal lath is erected on angle irons at the required distance from the outer wall and coated on the outside with one or more coats of portland cement plaster, to which a small amount of Sil-O-Cel powder, approximately 20 percent by volume, has been added to

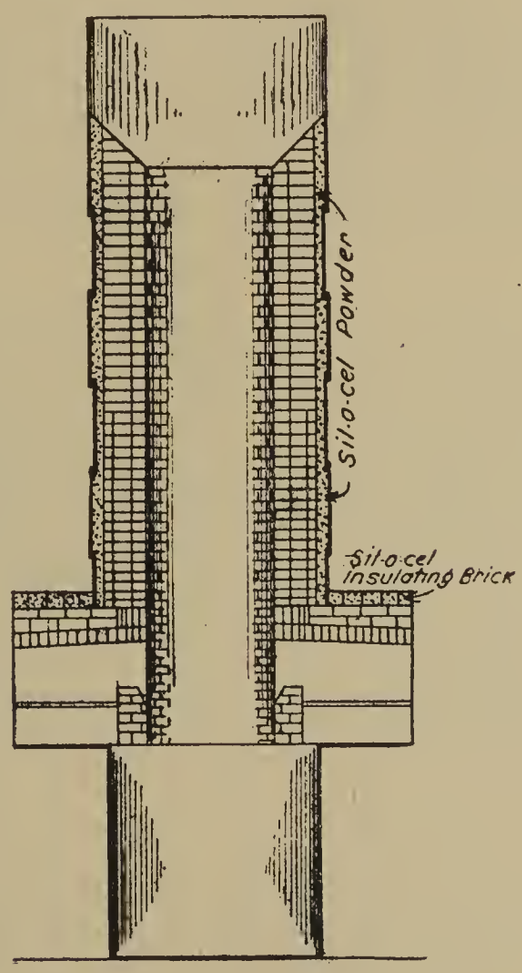

Fig. 6. Lime Kiln Insulated with Sil-O-Cel Powder.

give greater plasticity and ease of working and to increase the heat-resisting properties of the cement. Sil-O-Cel powder is packed to a density of 12 lb. per cubic foot between the brick wall and the expanded metal lath. This form of construction is relatively inexpensive and allows of as much insulation as is required, and furthermore gives an absolutely permanent surface of excellent appearance, which can be applied to almost any character of equipment.

A layer of pulverized material between the brick lining and furnace shell is the form of insulation most generally used in high-temperature metallurgical equipment, such as kilns of all kinds, gas generators, producers, stoves, etc.; in fact, it is universally applicable where the furnace has a suitable shell. In cases where support is required from the shell or setting, a denser variety of Sil-O-Cel which is not compressible, has been found to be effective. The denser product does not possess the unusually high insulating values of the natural Sil-O-Cel, but offers mechanical advantages for certain construction.

These four forms of construction can be modified to give walls of any desired thermal efficiency, the respective methods being

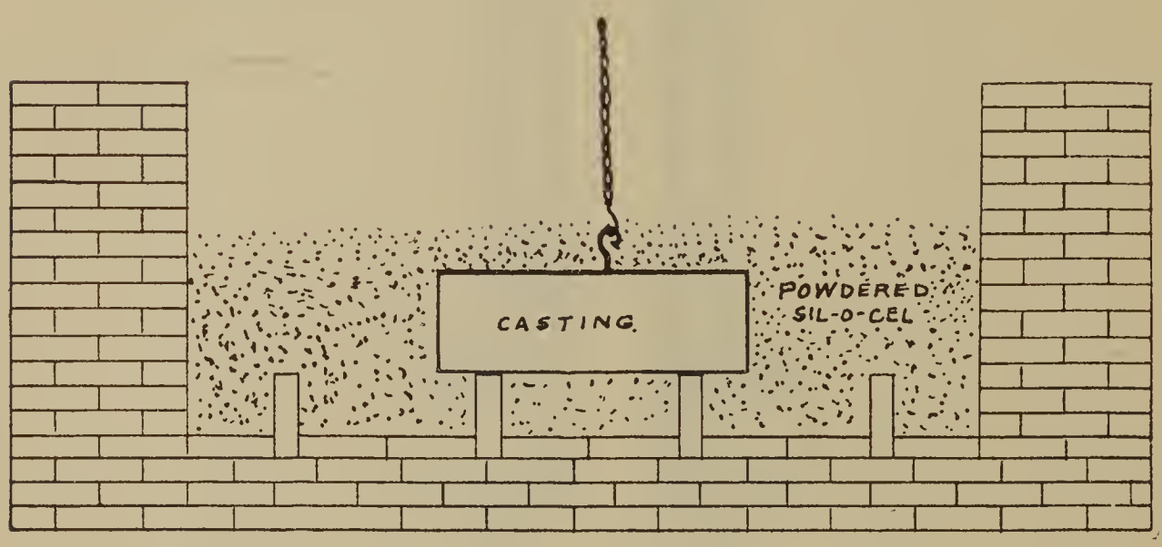

Fig. 7. Annealing Pit Containing Powdered Sil-O-Cel for Slow Cooling of Castings.

largely determined by the character of the work under consideration. Specific forms of high-temperature equipment are shown in Figs. 4 to 8.

In reverberatory furnaces Sil-O-Cel has found application as an insulating material for roofs and furnace walls in the manner indicated in Fig. 4.

Fig. 5 indicates the method which is finding universal application for gas-making equipment, showing the powdered Sil-O-Cel tamped between the firebrick lining and the metal shell to a density of about 12 lb. to the cubic foot (200 g. per cub. dm.). This form of construction has been in actual use for a number of years in some of the largest gas plants on the Pacific Coast, in

insulating oil-gas generators, superheaters, carburetors and similar equipment. The advantages of Sil-O-Cel in this connection are threefold: In the first place, the heat conducted to the surface of the metal shell which is dissipated by radiation and convection is reduced to a minimum. Secondly, in preventing the access of high temperatures to the steel shell, it prevents oxidation and deterioration of the shell through overheating and gives it the protection which it should have. Thirdly, Sil-O-Cel in the powdered form is to a certain extent elastic, allowing variation in expansion and contraction between the firebrick and the shell, eliminating all danger of excessive mechanical strains being set up between the two.

The insulation of lime kilns and similar equipment is shown in Fig. 6.

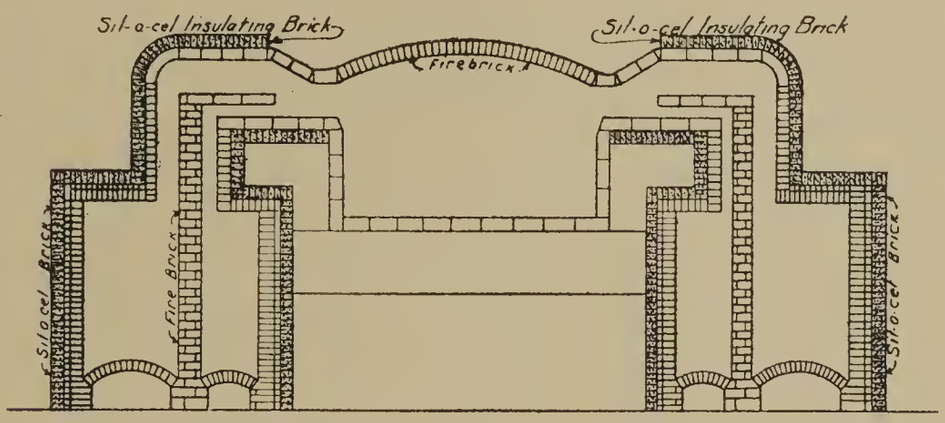

Fig. 8. Glass Furnace Insulated with Sil-O-Cel Brick.

A unique application of the use of powdered Sil-O-Cel in annealing castings and other heat-treated metal forms is illustrated in Fig. 7, which shows an annealing pit partly filled with Sil-O-Cel powder, in which the castings are placed or suspended by chains until they are cooled to the proper degree for working. The annealing pit is built of brick and the depth of powdered Sil-O-Cel which is used is determined by the size and shape of the castings to be annealed and the rate at which cooling is desired. This form of annealing eliminates to a very large extent the elaborate and costly annealing furnaces which are used in a great many plants and bids fair to become one of the most important uses of powdered Sil-O-Cel. This material has also been used as a packing material in boxes in which the metals to be heat treated are placed, the entire box being heated and allowed to cool slowly.

Glass furnaces insulated as shown in Fig. 8 are considerably more effective and economical than those operating without insulation.

Before leaving this subject, it would be well to again mention the fact that no attempt has been made in this presentation to cover all the fields of high-temperature work, but merely to outline the methods which are applicable to almost any form of high-temperature equipment.

DISCUSSION.

President L. Addicks: There are one or two comments I would like to make. It does not seem to me that the role played by convection in carrying heat from one surface to another has been brought out. Cellular construction confines this movement. Also this question of the installation on the top of a reverberatory furnace, that Mr. Krieger mentions, where it stopped the cooling. We have more than the question of overheating there. We have another complex question there entirely apart from the necessity of not carrying the brick above a certain temperature, in that we must not allow acids and bases to come together above a certain temperature.

J. W. Beckman: I would like to ask what it is that cements together the individual little cells in this material. I would also like to know how the material stands up in the presence of acids and alkalies.

Mr. Krieger: The material is formed or composed of myriads of lace-like diatoms. They are so small that the naked eye cannot discern them. It takes a powerful microscope. The diatom lives in salt and fresh water. On the Pacific Coast there must have been an abundant life of the diatom, because these beds that are still in existence in southern California are fully a thousand feet thick, and are hard and strong, standing a pressure of more than four hundred pounds to the square inch. They must have been many ages in forming and have been packed firmly together as the strata shows. Undoubtedly the action of the sea has had much to do with placing them in their present position. The sam-

ples shown are typical of the entire deposit as it was formed at the bottom of the sea. Once this structure has been destroyed it is impossible to reconstruct it without artificial bonding materials. It is the action of the diatoms settling in the ages that have gone that has bonded this mass together.

MR. BECKMAN: There is no cementing at all?

MR. KRIEGER: No cementing at all. The diatoms simply lie alongside of each other. Once you have destroyed their position you cannot get them back. There is no chemical action by acids except hydrofluoric. It disintegrates and dissolves in strong alkali.

SECRETARY J. W. RICHARDS: This paper has interested me very much and must interest all those who use furnaces and are concerned with saving heat. A general statement in connection with fuel-fed furnaces is that from fifty to ninety percent of the heat generated passes away with the gases from the furnace, while from ten to fifty percent of the heat generated is lost in conduction or radiation from the walls. There is, then, the possibility of saving from ten to fifty percent of the heat which is generated in the furnace by proper heat insulation of the walls. In electric furnaces, however, the problem is still more important. The gases which are generated in the electric furnace will carry out of the furnace only from ten to fifty percent of the energy generated within the furnace, and the loss from radiation may amount to from fifty to ninety percent of the total energy put into the furnace. Therefore, the study and proper utilization of these heat insulating materials concerns from fifty to ninety percent of the energy which is used for running electric furnaces, and is one of the most important items which the furnace manager can study and experiment upon.

KENNETH SEAVER: A point which I think may possibly bear a little more emphasis, although it has already been brought out by Mr. Krieger, is that of the insulation of furnaces where the heats are exceptionally high, such for instance as a typical heating furnace. I mention this because of some rather sad experiences along these lines. In one instance I have in mind, a heating furnace was installed with a few inches of sand over the roof in order to reduce radiation. The result was the collapse of the furnace roof after but a few days' run. After the layer of sand

was removed the same brick gave a normal life of six to eight months in this particular furnace. This instance is referred to only as suggestive and in no way with the aim of belittling the necessity and importance of proper heating insulation.

Mr. Krieger: There is an interesting case here in the city. The engine room and boiler room were close together and were very hot and uncomfortable. The engineer installed a set of these bricks as a matter of protection for his men. He put up a single layer of bricks on end so that he got two and a half inches (6 cm.) of insulation. He kept a record of the saving and declared that it amounted to two and a half percent of his fuel bill, or $140 a month. He used ten thousand bricks to accomplish this. In about three months he will have his money returned to him. That is a typical instance of high-grade insulation.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, at a Joint Session with the American Institute of Mining Engineers, September 17, 1915, President L. Addicks in the Chair.

THE ELECTROLYTIC PRECIPITATION OF GOLD, SILVER AND COPPER FROM CYANIDE SOLUTIONS.

By G. H. Clevenger.

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INTRODUCTION.

The present unsettled condition of the metal market, more particularly as regards zinc, which is used now almost exclusively as a precipitant in the cyanide process, makes a consideration of electrolytic precipitation, which is apparently the most feasible substitute, of particular interest at this time.

The electrolytic precipitation of gold, silver, and copper from cyanide solutions in connection with the cyanide process of gold and silver extraction, has frequently been the subject of satisfactory laboratory experiment, but much less frequently of successful commercial application. This comes about through the fact that experiments carried on for a few hours in the laboratory give no true indication of the life of anodes, formation of by-products, etc., to be expected in continuous operation. My purpose in presenting the present paper is not to give a theoretical discussion of the subject or to make new proposals for improved types of electrolytic precipitation apparatus, but rather to describe the few commercially-successful installations which have been made, calling particular attention to the difficulties which have arisen in their operation, in the hope that it may prove

useful to those who have to do with the installation of electrolytic precipitation equipment. In order that those of our members who are not familiar with the cyanide process may properly appreciate the peculiar and difficult problem which the complete precipitation of gold and silver from dilute cyanide solutions presents, I will digress sufficiently to make this clear before taking up the description of the various attempts to solve the problem. The solutions which are precipitated in present-day cyanide practice may contain a great variety of compounds arising from the decomposition of the cyanide, as well as from its combination with elements occurring in the ore treated, or introduced by chemical methods of precipitation. The principal constituents of such solutions, if zinc precipitation were not used, would be: simple alkaline cyanides, alkaline hydrate, gold and silver, and copper if it occurs in a soluble form in the ore undergoing treatment. The proportion of these various constituents present, particularly of the gold and silver, is extremely small compared with the amounts of metal present in solutions made by extraction processes in other industries.

In general the simple alkaline cyanide, as indicated by the Liebig titration test, will range in present-day practice from a trace to 0.25 percent, or a maximum of 1/400 of the solution. In certain cases of sand treatment of silver ores stronger solutions are used, but in general the cyanide strength of the solutions precipitated will fall well below the upper limit given. The alkali generally added is lime, although caustic soda has been used. There is rarely over 100 points present and most generally much less than this, and in some cases practically no protective alkalinity. (100 points of alkali correspond to a saturated solution of lime in distilled water at 20° C., *i. e.*, 0.13 percent.) The proportion of alkali present is therefore in many cases less than the cyanide. The gold present will range from nothing to 0.5 ounce (15.6 grams) per ton, and the silver from a trace to 10.0 ounces (292 grams) per ton. In general the proportion of gold and silver in solution is much less than the upper limits given. The grade of the ore treated does not always form a safe criterion of the gold and silver content of the solution, for the reason that the ratio of the weight of solution used to the weight of ore treated, or, as it is generally termed, "the

dilution," varies greatly, but in general, as might be expected, is greater with high-grade ores. Thus, if three tons of solution are used in treating one ton of ore, we have a 3 to 1 dilution, and the recoverable value of the ore has been transferred to 3 parts of solution, the average value of which would be ⅓ of the recoverable value of the ore treated; or, to take the concrete case of an ore assaying 0.50 oz. (15.6 g.) of gold per ton (approximately $10.00 per ton) from which 90 percent of the gold can be extracted by cyanide solution, there would be dissolved by the solution 0.45 oz. (14.0 g.) ($9.00) per ton of ore treated. With a 1 to 1 dilution the average content of the solution per ton would be 0.45 oz. (14.0 g.) ($9.00); with a 3 to 1 dilution the average content of the solution per ton would be 0.15 oz. (4.4 g.) ($3.00); with a 5 to 1 dilution the average content of the solution per ton would be 0.09 oz. (2.6 g.) ($1.80). It will, therefore, be apparent that this stage of the cyanide process, the transference of the gold and silver from the solid state as occurring in the ore, to the liquid state as dissolved in the cyanide solution, is unlike most other steps in metallurgy, which are in general to successively concentrate the metal sought into a smaller weight of material. Exceedingly small as is the proportion of gold and silver present in ores which it is possible in present-day practice to profitably treat by cyanidation, the proportion of gold and silver in the solutions requiring precipitation are generally still smaller. Perhaps a clearer idea of the small amount of metal involved, particularly in the case of gold, will be obtained by expressing the proportion fractionally. In solutions containing 0.50 oz. (15.6 g.) of gold per ton (approximately $10.00), an unusually high proportion, the gold would form 1/58,332 part of the solution. In the case of waste solutions, which are or should be precipitated before they are discarded, it is not unusual to deal with solutions containing less than 0.01 oz. (0.31 g.) of gold per ton (20 cents), or only 1/2,916,600 of the total weight of the solution. Tail solutions containing only 1 or 2 cents values per ton are regular practice at many mills using zinc dust precipitation.

At the present market price of silver (about fifty cents per ounce) there would be required about forty times the weight of gold present to give an equivalent value in silver. Therefore,

in the treatment of silver ores a much greater weight of metal would be involved, but still the relative proportion of metal to the total weight of solution is small. As gold and silver most frequently occur associated, the absolute weight of metal to be precipitated will depend upon the ratio of these two metals in the ore treated. The greater weight of metal involved in the treatment of silver ores or ores in which silver predominates, perhaps in a certain measure explains the greater ease with which solutions resulting from the treatment of such ores are handled by all precipitation processes.

Copper in solution is an incident of gold and silver extraction, as at present there is no effort made to recover copper in this way; however, this is an interesting possibility, and would be feasible provided the cyanide combined with the copper could be economically regenerated. In many cases the proportion of copper in solution will be less than that of the gold and silver, and, so far, even with electrolytic precipitation, there has been no serious attempt to treat gold and silver ores by the cyanide process unless the proportion of readily soluble copper was considerably below 1.0 percent. The interference of copper with other methods of precipitation, as well as its prejudicial effect upon extraction, make a consideration of its behavior with electrolytic precipitation of particular interest, but beyond the province of the present paper.

The electrolytic precipitation of gold and silver from cyanide solutions, therefore, involves the practically total precipitation of an extremely small weight of metal from solutions containing a comparatively small proportion of soluble salts, and which are therefore poor electrical conductors. The fact that the alkaline cyanides are readily decomposed by electrolysis and that the economy of the cyanide process depends upon the continued re-use of the solvent make it imperative to precipitate with the minimum decomposition of cyanide, and preferably with a regeneration of cyanide. The difficulty of the problem at best will therefore be apparent.

SIEMENS-HALSKE PROCESS, ON THE RAND, SOUTH AFRICA.

The precipitation of gold and silver from cyanide solutions by electrolysis, employing a soluble anode of the metal to be

deposited, had been practiced in electroplating long before the complete precipitation of gold and silver from the dilute solutions resulting from ore treatment was attempted by electrolysis, using an insoluble anode. In 1887 a British patent was granted on the MacArthur-Forrest process of gold and silver extraction, involving the use of dilute solutions of potassium cyanide and zinc precipitation. In the same year, Dr. Siemens, working independently and acting upon observations made at his plating plant at Berlin, Germany, taken together with the statements of chemical authorities that gold was soluble in solutions of the alkaline cyanides, developed a process of gold and silver extraction involving the use of dilute solutions, more dilute than those at first used with the MacArthur-Forrest process, and electrolytic precipitation. In the course of this work zinc filings had been tried as a precipitant, but with the very dilute solutions employed electrolytic precipitation proved more satisfactory. The first experimental plant was erected at Siebenburgen for extracting gold from concentrates, and although the process was in successful operation as early as 1888 in other mining localities it was not until a number of years later, in 1893, that the Siemens-Halske process was introduced into the Rand gold field of South Africa.

On the Rand, at first, only the sand portion of the ore pulp resulting from the stamp-crushing and plate-amalgamation process could be successfully treated by cyanidation, as leaching was the only method of treatment then in use. The solutions resulting from sand treatment contained sufficient free cyanide to give satisfactory results by ordinary zinc-shaving precipitation, as then practiced. This method of precipitation was, therefore, almost universally used for these solutions. With the advent of the decantation method of treatment for the unleachable portion of the pulp, which had previously been allowed to accumulate on account of not being amenable to treatment by leaching, the problem at once arose of precipitating from large volumes of solution which were weak in both cyanide and gold on account of the high dilution necessary in treating slime by the decantation method. At this time the ordinary zinc-shaving method of precipitation did not give satisfactory results when used with very weak solutions. The Siemens-Halske electrolytic

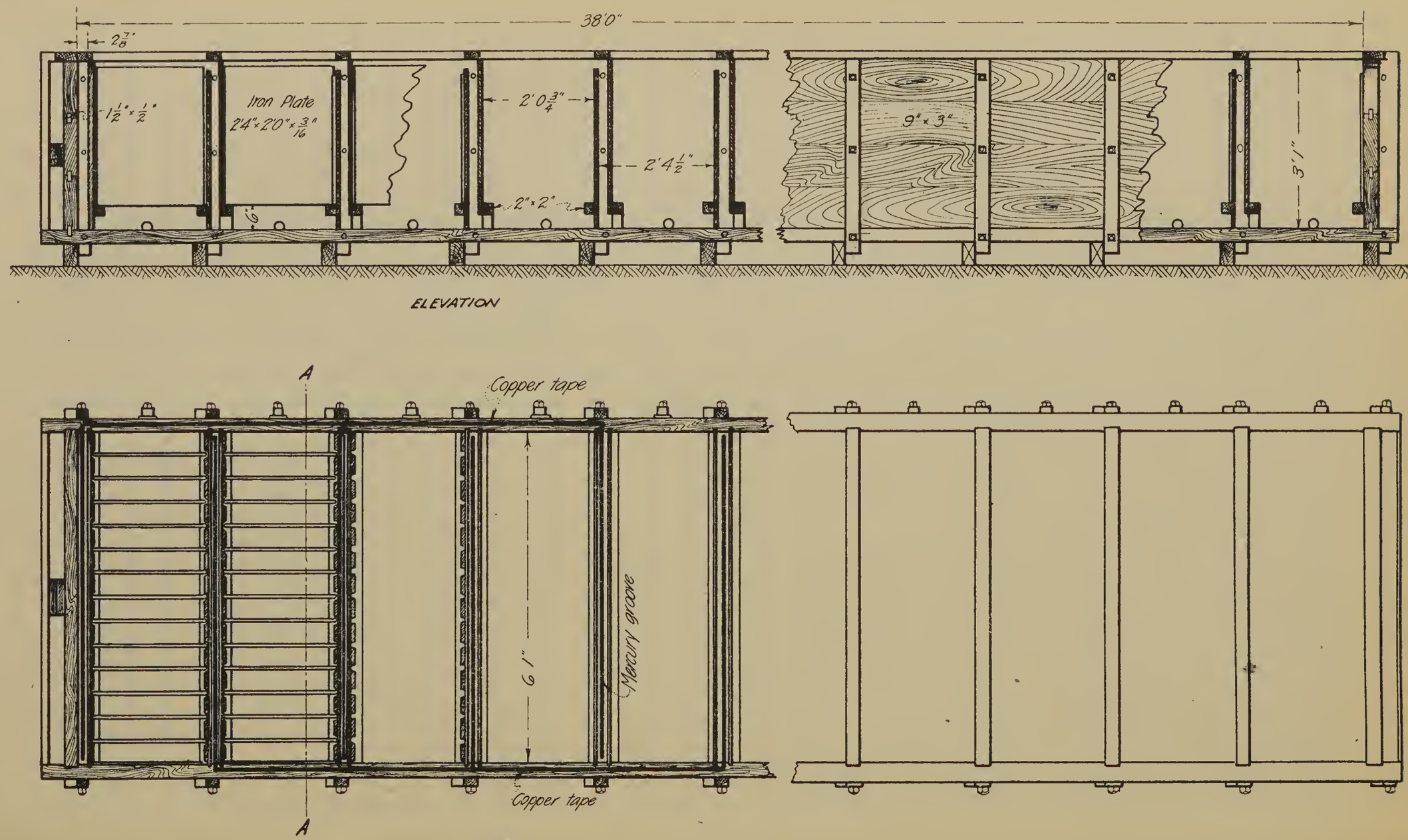
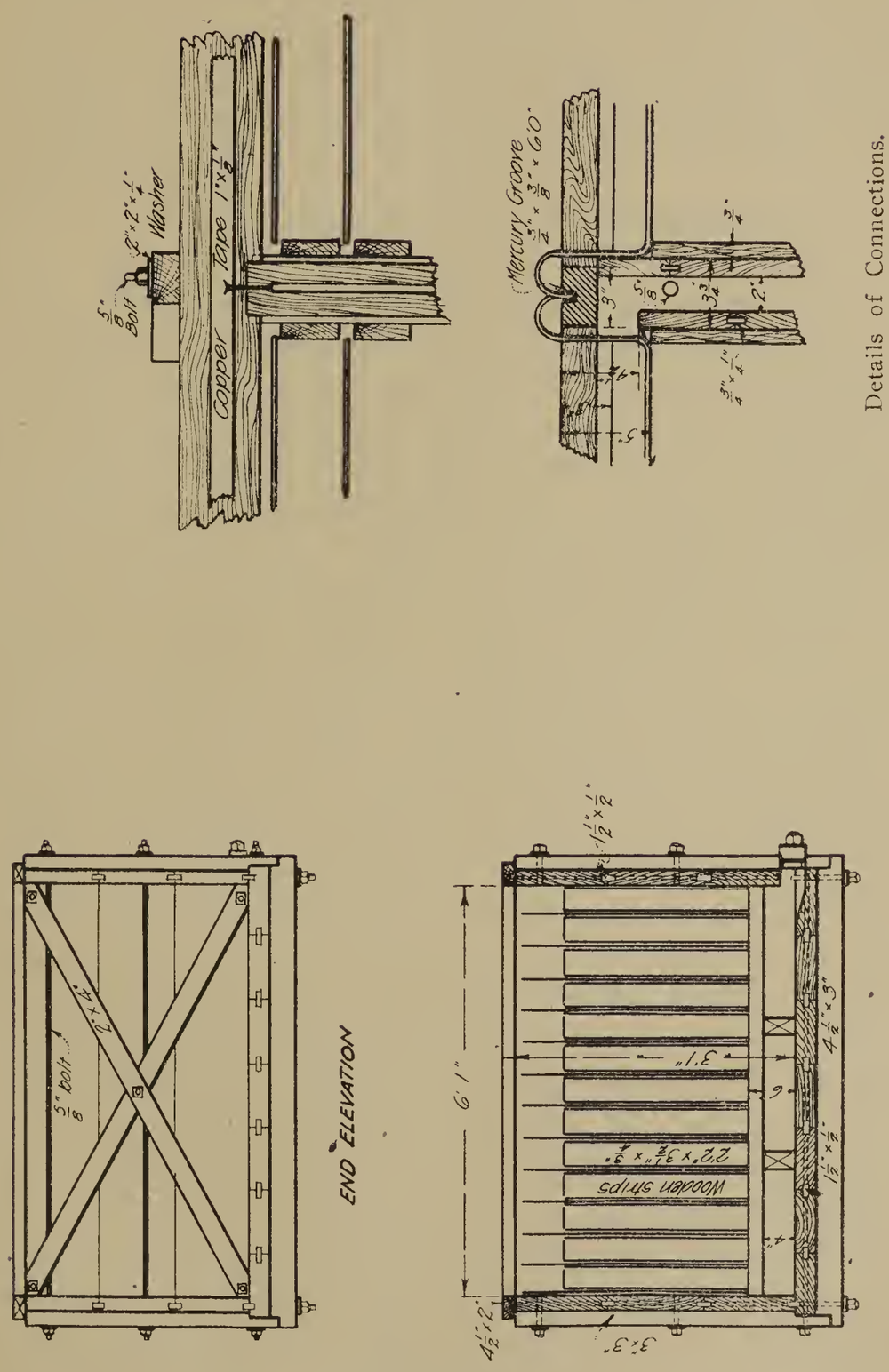


FIG. 1. Siemens-Halske Process.



Siemens-Halske Process (Details of Fig. 1). (Note: Cathodes not in place.)

process of precipitation, therefore, came into very general use for precipitating the solutions resulting from slime treatment.

The Siemens-Halske process was first introduced at the Worcester mine. Installations at other mines rapidly followed until at one time there were about twenty in operation on the Rand. In the Siemens-Halske process, iron anodes ⅛ to ¼ inch (0.3 to 0.6 cm.) thick, and lead-foil cathodes about 0.00032 inch (0.0008 cm.) thick were used. In general, the anodes and cathodes were set vertically and about 1½ inches (4 cm.) apart. There was considerable variation in the size and arrangement of the anodes and cathodes. At the Worcester plant they were 7 feet long by 3 feet wide (2.1 x 0.9 m.), but in later installations, to facilitate handling, they were made smaller, as shown in Fig. 1. The anodes were enclosed in sacks of textile material for the twofold purpose of preventing short circuits and of collecting the prussian blue and iron oxide formed from the iron anodes.

The lead-foil cathodes were frequently cut in narrow strips for the purpose of increasing the surface. These were strung upon iron wires mounted in light wooden frames. Another expedient which gave still greater surface was to cut the lead into shavings similar to zinc shavings. These were packed into the space between the covered anodes. Various arangements of the precipitation units were tried, but the one which seemed to be the most favored was to construct the containing box as shown in Fig. 1, with alternate wide and narrow compartments, the narrow compartments serving for the down-flow of the solution, while the anodes and cathodes were suspended in the wide compartments, through which the solution had an upward flow. This general arrangement will be recognized as being similar to that of the boxes used for zinc-shaving precipitation. The current density used was from 0.03 to 0.06 ampere per square foot (0.33-0.66 ampere per sq. m.) of anode surface. The aim was to obtain a coherent plating of the gold upon the lead cathodes. After sufficient gold had accumulated upon the cathodes (2 to 12 percent of their weight) they were removed, melted and the gold recovered by cupellation, either locally or at a central reduction plant.

There was a long and bitter controversy on the Rand regarding the relative merits of zinc and electrolytic precipitation. In

1898, Betty, by means of a drip of strong cyanide solution at the head of the zinc boxes, in conjunction with the zinc-lead couple, which was first proposed by MacArthur in 1894, demonstrated that zinc precipitation could be satisfactorily used for solutions low in both cyanide and gold. After satisfactory precipitation of these dilute solutions by zinc became possible, electrolytic precipitation rapidly lost ground and finally was entirely superseded by zinc precipitation.

PRACTICE AT MINAS PRIETAS, MEXICO.

E. Andreoli, early in 1895, while working with the Siemens-Halske process in South Africa, accidentally discovered the lead peroxide anode, and although the advantages of peroxidized lead over iron as an anode material were at once recognized, it does not appear to have been used to any extent in that locality, possibly for the reason that electrolytic precipitation, at the time that this development was announced, was being rapidly displaced by zinc precipitation. After investigating many possible cathode materials, Andreoli suggested iron as being the best on account of its cheapness, strength, and the firm adherence of the gold to it. Borchers, however, states that from the electrochemical standpoint the use of iron cathodes is theoretically incorrect. Andreoli proposed recovering the gold from the iron cathodes by dipping them in a bath of molten lead. The gold was to be recovered from the lead by cupellation. The iron cathode used in this way does not appear to present any advantage over the lead-foil cathode, as it also involved the use of lead and necessitated the operation of cupellation.

In 1899, Charles Butters, who had been prominently identified with the introduction of the Siemens-Halske process in South Africa, assisted by two former members of his staff, H. T. Durant and E. M. Hamilton, developed a new electrolytic precipitation process which was first successfully used for a number of years in connection with the cyanidation of a large deposit of pan-amalgamation tailing, and later of ore directly, from the mine at Minas Prietas, Mexico.

The original installation for electrolytic precipitation consisted of six wooden boxes, as shown in Fig. 2, 30 feet (9 m.) long by 10 feet (3 m.) wide and 5 feet (1.5 m.) deep, having a slope

of one inch to the foot (8 cm. to 1 m.) toward one side, to facilitate the removal of precipitate. The boxes were divided by wooden partitions into alternate wide and narrow compartments, twelve of each. The partitions were so arranged as regards the bottom that the narrow compartments throughout the box served only for the downflow of the solution, whilst the wide compartments, in which were suspended the anodes and cathodes, served for the upward flow of solution. This general arrangement of the compartments is the same as that used with the

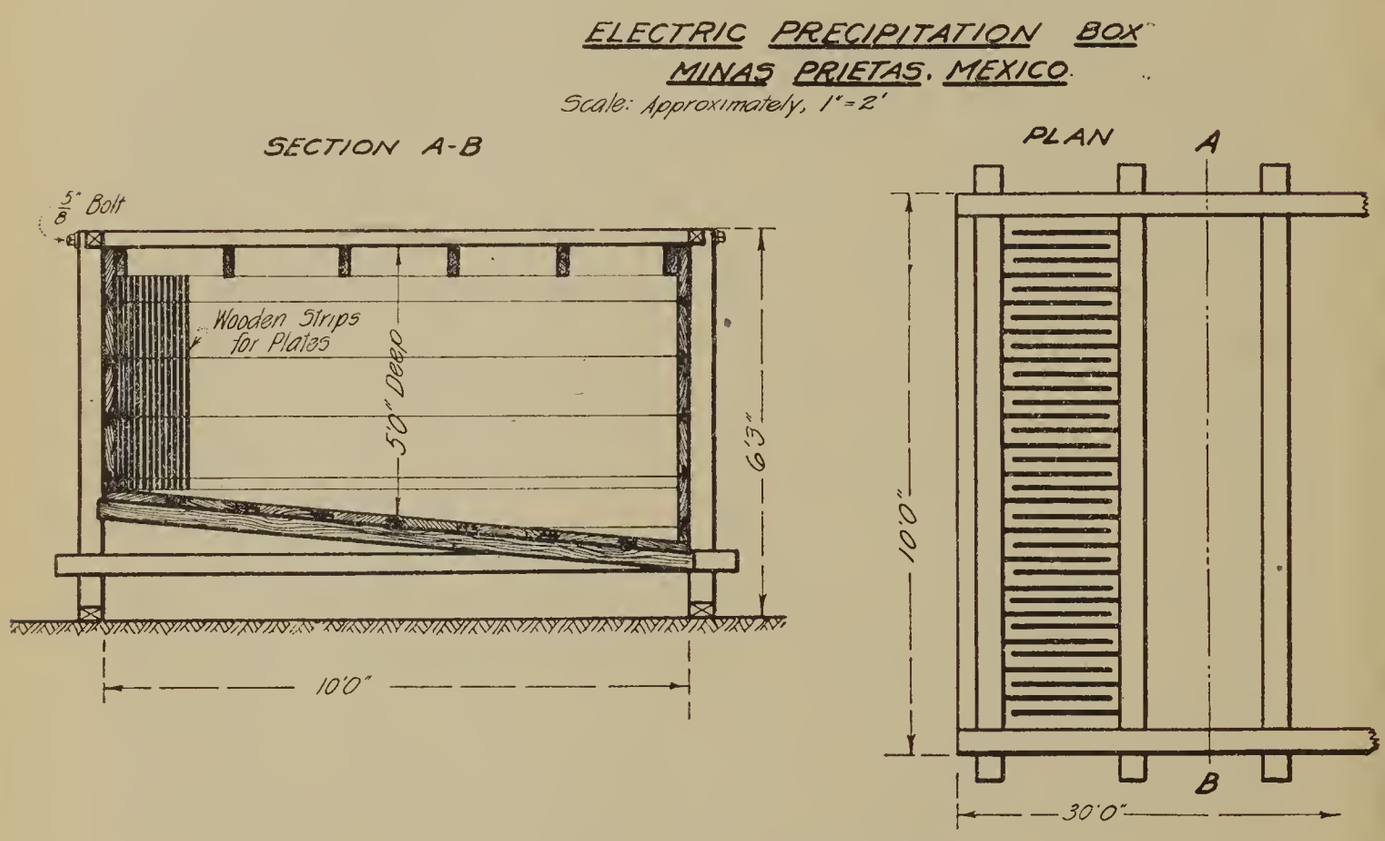


FIG. 2. Practice at Minas Prietas, Mexico.

Siemens-Halske process. Each wide compartment was fitted with 18 lead anodes, 48 in. x 22 in., coated with lead peroxide, formed by electrolysis in a special cell, and 17 cathodes composed of lead foil, cut in strips, strung upon wires supported by wooden frames similar to the cathodes used with the Siemens-Halske process in South Africa. The current was supplied by two Siemens-Halske dynamos, each capable of developing 250 amperes at 30 volts, feeding into copper bus bars 1¼ x ¼ inches (3.1 x 0.6 cm.) laid on top of the boxes. In order to insure good contacts, the wires leading from the individual anodes and cathodes were soldered to the bus bars, mercury-cup

contacts having proved unsatisfactory. The solution passed through three sets of boxes, each set comprising two boxes set in tandem. One set of two boxes was used for precipitating the solution resulting from sand treatment and two sets of four boxes for precipitating the solution resulting from slime treatment. The current density was so regulated that the metals were deposited as a flocculent precipitate which largely fell to the bottom of the compartments in the form of a fine slime, as in zinc-shaving precipitation, rather than as an adherent coating upon the cathodes as in the Siemens-Halske process. After a short period of operation, it was found that the precipitate did not all fall to the bottom of the box, but that part of it formed as a rather loosely-adherent mass on the cathodes. This necessitated washing and shaking of the cathodes when it was desired to make a complete clean-up. It was soon apparent that the fragile lead-foil cathodes could not long withstand such treatment, so an investigation was started with the view of finding a more satisfactory cathode. This resulted in abandoning the lead-foil cathode in favor of a cathode made from ordinary tin-plate, which possessed the necessary strength and from which the precipitate could be readily brushed without removal of the cathodes from the containing box.

The pan-amalgamation tailing cyanided at this plant resulted from the treatment by raw pan-amalgamation of a comparatively simple siliceous silver-gold ore. The tailing contained copper, mercury, and chlorides as a result of the chemicals added during amalgamation. After the tailing deposit had been exhausted, the low-grade ore which had been left in the mine was treated. The pulp was separated into sand and slime, the sand being treated by percolation and the slime by agitation, natural settlement and decantation. The volume of the solution precipitated varied as did also its metal content. The percentages of cyanide and alkali were less variable, but by no means constant. Below are given average figures covering two months' operation, for solutions resulting from sand treatment when pan-amalgamation tailing was being treated. Average amount of solution precipitated per 24 hours, 216 tons. Current density 0.55 ampere per square foot (5.9 per sq. m.) of anode surface. The voltage across the anodes and cathodes varied in the different compartments,

but averaged about 3. The head solution, or solution entering the precipitation boxes, contained: 0.147 oz. (4.57 g.) gold per ton; 3.51 oz. (109.2 g.) silver per ton, and 0.0792 percent of cyanide in terms of potassium cyanide. The tail solution or solution leaving the electrolytic precipitation boxes contained 0.013 oz. (4.04 g.) gold per ton; 0.29 oz. (9.02 g.) silver per ton, and 0.0938 percent cyanide. The gain in cyanide was 0.0146 percent. As there was used 1.2 tons of solution in treating each ton of sand, the cyanide apparently regenerated amounted to 0.35 lb. (0.16 kg.) per ton of sand. The percentage of gold precipitated was 91.0 and the percentage of silver precipitated was 91.7. No attempt was made to lower the gold and silver in the tail solution, as none of it was used for final washes.

The following are average figures covering the same two-month period for the precipitation of solution resulting from slime treatment: Average amount of solution precipitated per 24 hours, 480 tons. Current density 0.3 ampere per square foot (3.3 per sq. m.) of anode surface. The voltage across the anodes and cathodes averaged 2.6. The head solution contained: 0.055 oz. (1.71 g.) gold per ton; 1.45 oz. (45.1 g.) silver per ton, and 0.0409 percent cyanide. The tail solution contained: 0.0067 oz. (0.21 g.) gold per ton; 0.15 oz. (4.67 g.) silver per ton, and 0.0527 percent cyanide. The gain in cyanide was 0.0118 percent. As there was used 4 tons of solution in treating each ton of slime, the cyanide apparently regenerated amounted to 0.94 lb. (0.43 kg.) per ton of slime. The percentage of gold precipitated was 88 and the percentage of silver 89.6. When the solution flow was cut down to two-thirds normal, the tails contained 0.0025 oz. (0.77 g.) gold and 0.06 oz. (1.86 g.) silver per ton. The regeneration of cyanide was doubtless greater with the solution resulting from the treatment of the slime on account of the greater percentage of copper which it contained. When treating ore directly from the mine, which contained little or no copper, the regeneration was not sufficient to be detected by ordinary titrations.

PRACTICE AT SAN SEBASTIAN, SALVADOR.

The original electrolytic precipitation plant installed at Butters' Salvador Mines, San Sebastian, Salvador, was similar to

the Minas Prietas plant. However, after being placed in operation it was found necessary to modify the practice in several important particulars. The two wooden containing boxes used were 30 feet (9 m.) long, 10 feet (3 m.) wide, and 4 ft. 8 in. (1.4 m.) in depth. The bottom was given a slope to one side at the rate of one inch per foot (8 cm. per m.). Each box was divided into 12 compartments, 10 of which were used for precipitation, the last two merely serving as settlers. Each compartment contained 25 anodes and 24 cathodes. The anodes were rolled lead plates ⅛ inch (0.3 cm.) thick, 22 inches (56 cm.) wide and 48 inches (122 cm.) long. For some time the anodes were peroxidized in a special cell using an electrolyte consisting of 1 percent of potassium permanganate and 2 percent sulphuric acid; but later untreated lead plates were used. At first tin-plate cathodes similar to those used at Minas Prietas were tried, but certain difficulties arose which made it necessary to abandon the tin-plate cathode. The original intention was to deposit the gold and copper as a non-adherent slime, as at Minas Prietas, but despite the fact that a higher current density was used the gold and copper were deposited upon the cathodes as a firmly adherent coating. The predominating metal in the solution at Minas Prietas was silver, but at San Sebastian it was copper. The well-known fact that silver is very prone to give non-adherent coatings, while copper has a strong tendency to give adherent coatings, seems to offer a ready explanation of the difference in behavior of the precipitated metals at the two plants. The removal of the strongly-adherent copper-gold plating from the tin cathodes presented a most difficult problem. Various expedients for removing it were tried, such as heating the cathodes with a gasoline torch, scraping and pounding them, etc. After these various heroic measures had proved ineffective, it was decided to return to the lead-foil cathode cut into strips, as used in the Siemens-Halske process. When it was desired to "clean up," the lead-foil strips were removed, ground, and shipped to smelters for the separation of the metals. The current was supplied by a belt-driven Siemens-Halske dynamo giving 450 amperes at 30 to 35 volts. The current density was 1 ampere per square foot (10.8 per sq. m.) of anode surface, and the

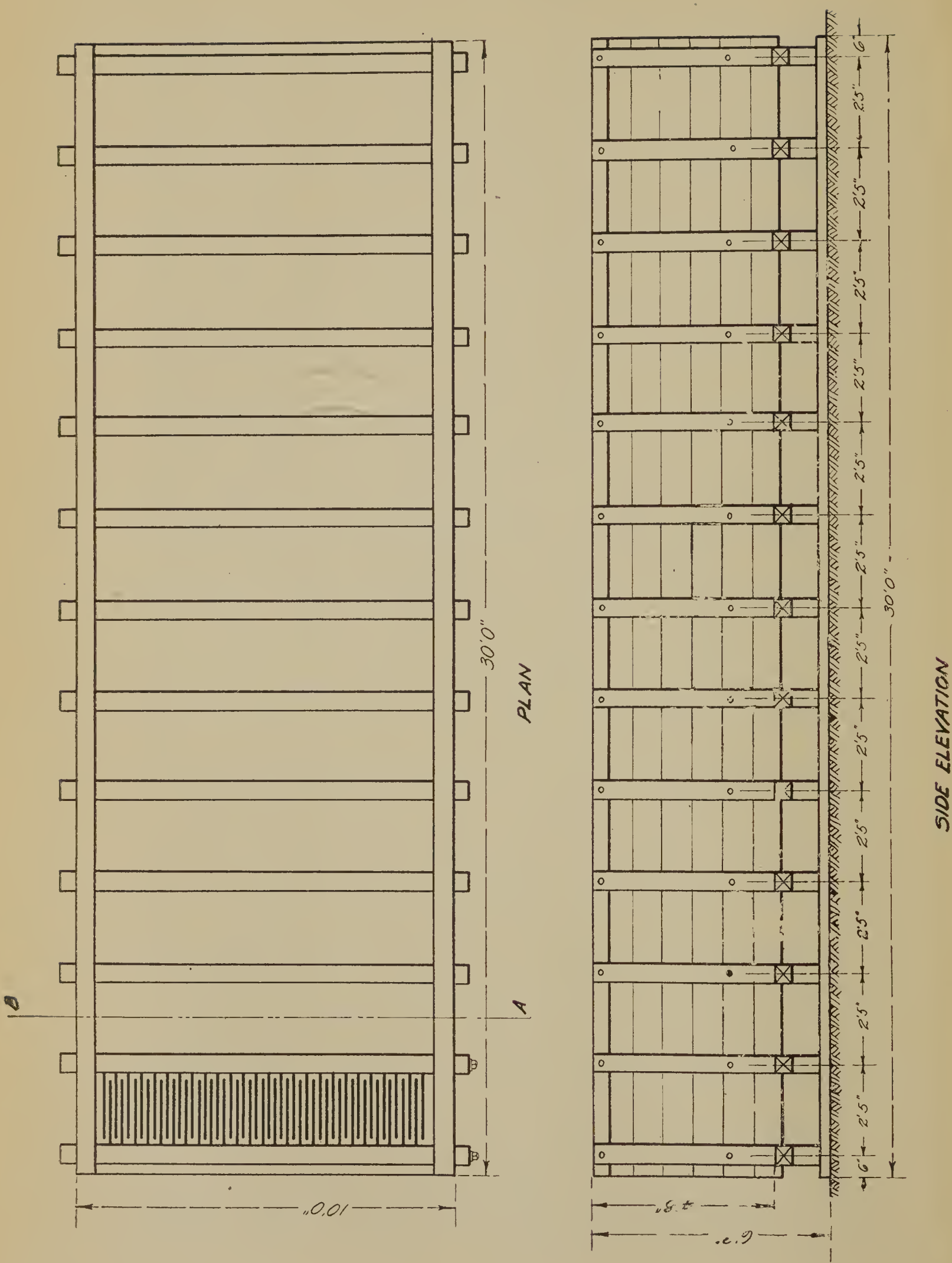
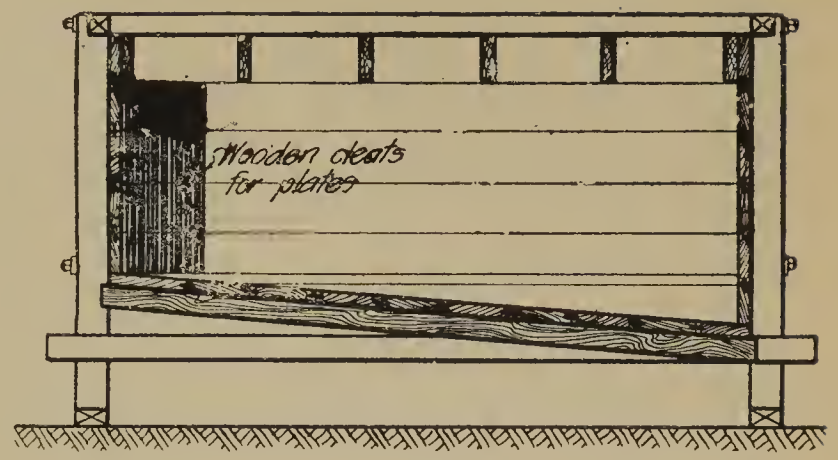
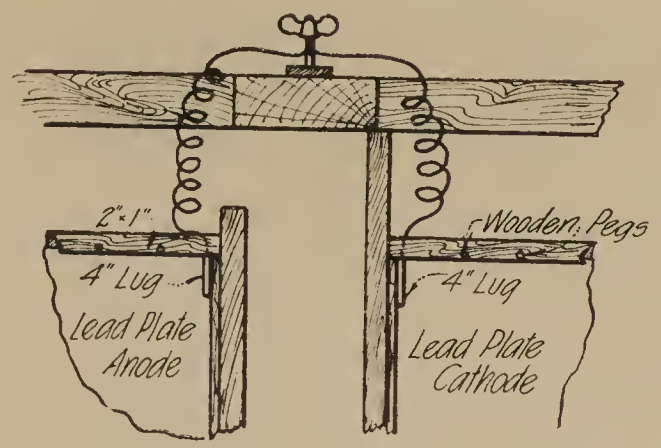
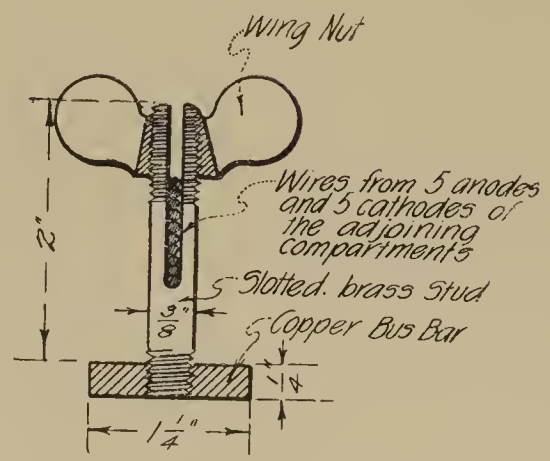


FIG. 3. Electric Precipitation Box, San Sebastian, Salvador.

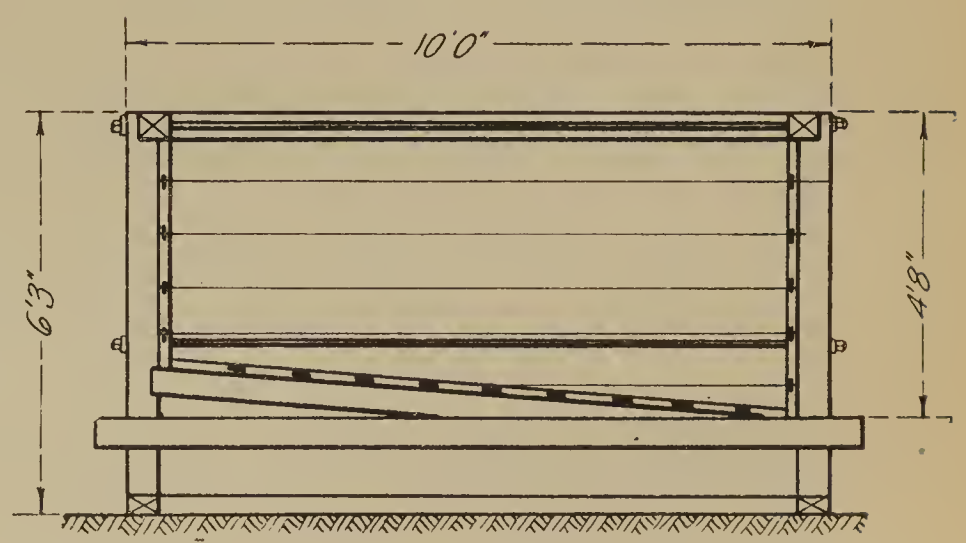
SECTION A-B







DETAIL OF CONNECTIONS



END ELEVATION

Electric Precipitation Box (Details of Fig. 3).

voltage across the anodes and cathodes in each compartment was 4 to 4½.

This general practice was continued until C. P. Richmond modified it so that the metals could be separated locally. The lead-foil cathodes were replaced by sheet-lead cathodes 1/16 inch (0.15 cm.) thick, 22 inches (55 cm.) wide and 48 inches (120 cm.) long, so arranged that they could be readily removed from the containing box. To this end, the connecting wires for the cathodes, instead of being soldered to the copper bus bars, were clamped by wing-nuts in split studs screwed into the bus bars. The general arrangement of the precipitation box is shown in Fig. 3. The wires from five anodes and cathodes of opposite compartments were laid in each slot and a tight connection secured by screwing down the wing-nut. The studs were spaced 19 inches apart and six of them connected the cathodes of one compartment to the anodes of the adjoining compartment. By this arrangement it was possible to remove any of the cathodes without interrupting the flow of current or solution. At San Sebastian it was found advantageous to operate so as to keep the concentration of the copper down to a point where it did not interfere with gold extraction, and precipitate the remaining gold by zinc shaving. This was done despite the fact that zinc was said to interfere with electrolytic precipitation in South Africa. The solution leaving the electrolytic boxes was divided between two zinc boxes each 22 feet (6.6 m.) in length and having 14 compartments, 2 feet (60 cm.) by 1 foot (30 cm.) and 2 feet (60 cm.) deep, filled with zinc shaving. The ore treated was a high-grade gold ore containing considerable pyrite and sufficient copper left in the soluble form after the roasting which preceded cyanide treatment, to occasion trouble in cyanidation unless electrolytic precipitation were used. The average gold content varied, but at the time that electrolytic precipitation was in use ranged from 2 to 4 oz. (62 to 124 g.) per ton. The soluble copper varied from ½ to 2½ pounds (0.23 to 1.14 kg.) per ton. The ratio of gold to copper in the electrolytic deposit ranged from 1 to 7 up to as high as 1 to 25, but generally was between the limits of 1 to 9 and 1 to 14. The average results of two months, taken at random, will give a general idea of the performance. During this period there was treated 45 tons

of ore daily, averaging 2.27 oz. (70.6 g.) gold per ton. Approximately 150 tons of solution was precipitated daily. The average content of the head solution was: gold 0.79 oz. (24.6 g.) per ton, copper 0.075 percent, cyanide 0.118 percent. The average content of the tail solution from the foot of the zinc box was gold 0.004 oz. (0.112 g.) per ton, copper 0.048 percent, cyanide 0.154 percent. The percentage of gold in the deposit at the head of the electrolytic box was about 7; at the foot of the box it was about 3. The current density was 1.0 ampere per square foot (11 per sq. m.) of cathode surface. The voltage across the anodes and cathodes of each compartment was 4 to 4½. During the treatment of the ore there was consumed 7.2 lb. (3.27 kg.) of sodium cyanide per ton. There was precipitated in the electrolytic boxes 1.5 lb. (0.68 kg.) of copper and apparently there were regenerated 1.92 lb. (0.87 kg.) of cyanide, in terms of potassium cyanide, per ton of ore treated. Eighty to 90 percent of the gold and most of the copper was precipitated in the electrolytic boxes. Passage through the zinc boxes brought the total percentage of gold precipitated up to 99.5. The zinc boxes precipitated little copper, despite the fact that the solution invariably contained copper at this point. Under normal conditions the percentage of copper in solution remained more or less constant, any increase through contact with the ore being precipitated by the electrolytic boxes. When the copper built up in the solution, as was sometimes the case through treating ore containing an unusually high percentage of copper, the bad effect was at once noted upon the gold extraction.

Electrolytic Refining of the Cathode Deposit.

After the cathodes had remained in the precipitation boxes 20 to 30 days, during which time they had increased in weight from 8 to 12 pounds (3.5 to 5.5 kg.), they were removed and, after draining, were connected as anodes in a special electrolyzing cell shown in detail in Fig. 4, containing an electrolyte of 2 to 3 percent sulphuric acid, which was thrown away when its strength was reduced to 1 percent. They were here enclosed in compartments so constructed as not to interfere with the free passage of the current, and which served to collect the gold slime freed by solution of the copper of the deposit. The com-

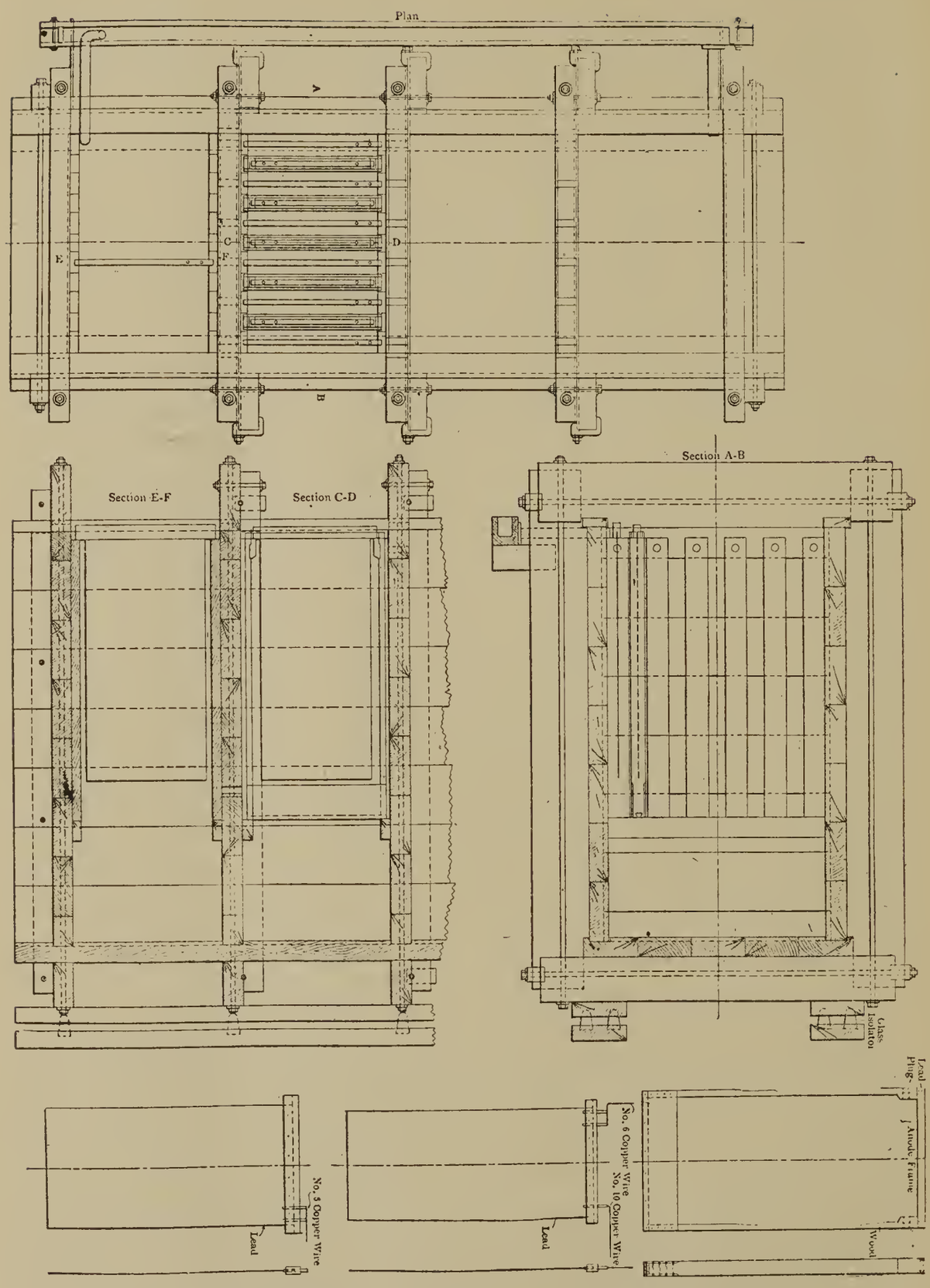


FIG. 4. Acid Refining Tank, with Details of Anode and Cathode.

partments consisted of a wooden frame having a pocket at the bottom somewhat larger than the cathode plate, covered on both open sides with cotton twill held in place by tacking. The cathodes used in the refining boxes were lead plates $\frac{1}{16}$ inch (0.16 cm.) thick, 22 inches (55 cm.) wide and 48 inches (120 cm.) long. The refining box contained four compartments, each holding 5 anodes and 6 cathodes. The spacing between the plates was 4 inches (10 cm.). The compartments were connected in series and received a total current of 450 amperes. The average voltage across the electrodes of each compartment was 8. The current density was approximately 5 amperes per square foot (55 per sq. m.) of anode surface. The copper was deposited at the cathode as a flocculent non-adherent precipitate, which collected in the bottom of the main cell, while the gold slime remained inside of the cloth-sided compartments surrounding the anodes. When the operation had proceeded to the point where all of the copper of the copper-gold deposit was dissolved, the anode plates were removed, washed, and replaced again in the regular precipitation box as cathodes. The time required for dissolving the deposit on a plate was from 48 to 72 hours. Two electrical connections were provided for each cathode; one, a No. 10 copper wire, used when the plate functioned as cathode in the regular precipitation box, and the other a No. 6 wire, which was used for carrying the heavier current employed in the refining cell. Both wires were permanently soldered to the lead lugs cast on the plate. Beginning at the head of the precipitation box, the cathodes were removed and, as refined, replaced, thus gradually working down toward the foot of the precipitation box. By the time that the foot of the box was reached, the cathodes at the head were again ready for refining. The total time of "cleaning up" a precipitation box was from 25 to 30 days. Consequently the operations of cleaning up and refining were going on almost continually. The solution in the acid refining box was circulated by a lead air-lift. The interval between "clean-ups" of the refining box varied from 15 to 25 days, depending upon the quantity of copper which had accumulated at the bottom of the cell. The copper capacity bore a definite ratio to that of the anode compartments, so that when the former was full the latter was about three-quarters filled. By this time the twill

sides of the receptacle were so weakened by the acid that they required replacement. When it was desired to "clean up" the refining box, the acid electrolyte was siphoned into a storage tank and the anode receptacles were raised and allowed to drain over the refining box. They were then placed in an upright position upon a washing board supported above a tank provided with a filter bottom, the twill was cut down the sides, removed, and the gold slime washed into the tank. The wooden frames were well scrubbed and the twill washed over the same tank, after which it was burned in a dryer. When thoroughly drained, the gold slime was removed from the tank, dried and united with the ashes from the twill. After mixture with the proper fluxes it was melted in graphite crucibles heated in an oil-fired furnace. The buttons resulting from the preliminary melts were combined, remelted and cast into bars 700 to 800 fine for shipment. The copper slime was flushed through 1½ inch (4 cm.) holes bored in the side of each compartment one inch (2.5 cm.) above the bottom into a cement launder in the floor which conveyed the slime outside the building to a tank provided with a filter bottom. After draining and drying it was sampled and boxed for shipment. The dried copper precipitate contained 84 to 87 percent metallic copper and 1.82 to 3.72 oz. (56.6 to 115.7 g.) gold per ton. The total time required for a clean-up was 7 hours. A number of years ago, when this system of refining was in operation, the net returns from the copper more than paid all the expense of refining, melting the gold and shipping the copper.

PRACTICE AT VIRGINIA CITY, NEVADA.

In the installation of the electrolytic precipitation plant at Virginia City, Nevada, Messrs. Chas. Butters & Co., Ltd., had the benefit of the experience gained at the plants previously installed on the Rand, South Africa, at Minas Prietas, Mexico, and at San Sebastian, Salvador. This resulted in several quite important improvements. Originally, there were nine boxes, similar to that shown in detail in Fig. 5, the plan being to use three of these boxes for precipitating copper from a preliminary wash by sulphurous acid, which, when the plant first began operations, was intended to precede cyanide treatment. The other six boxes were to be used for precipitating gold and silver, together with

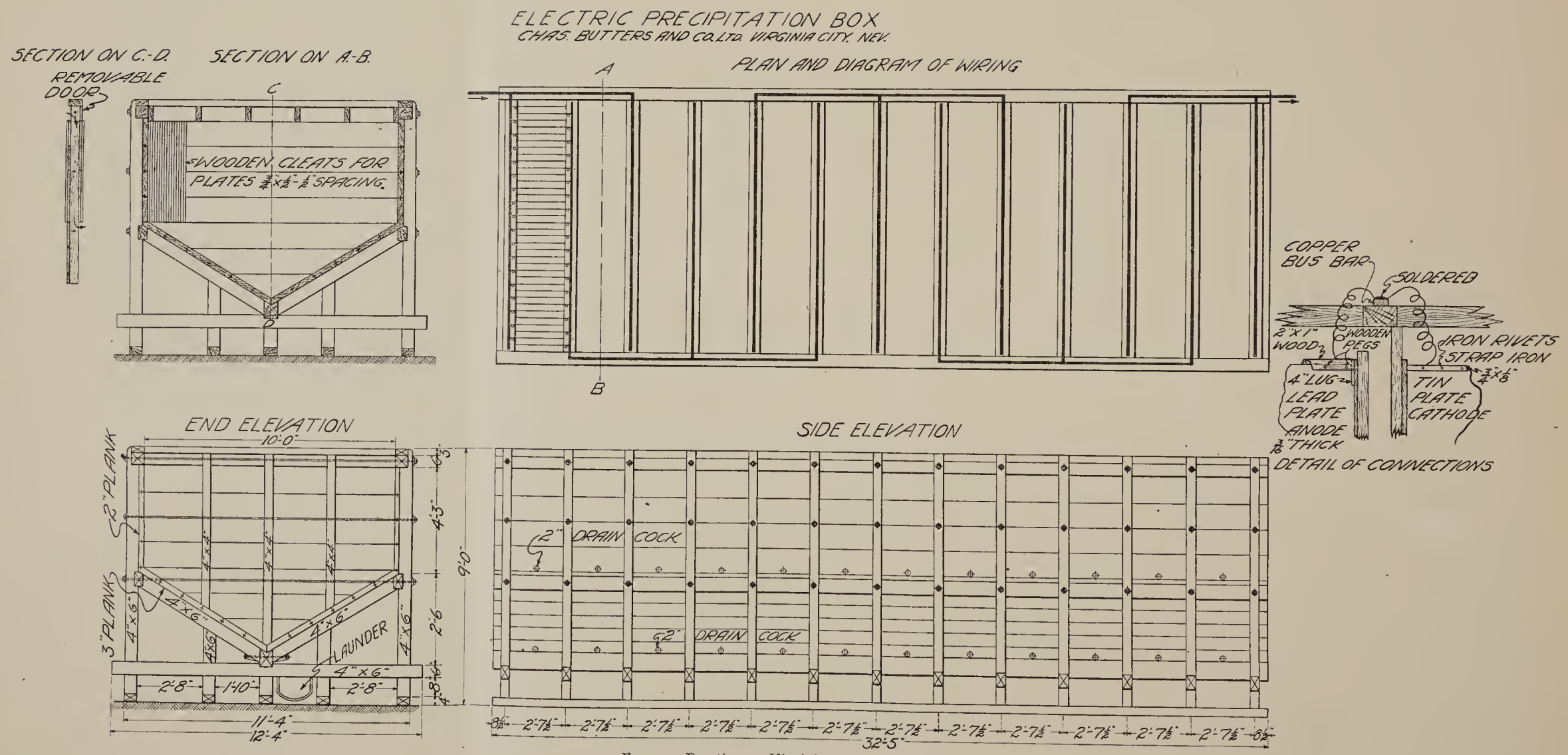


FIG. 5. Practice at Virginia City, Nevada.

any remaining copper from the cyanide solutions. The preliminary treatment with sulphurous acid was finally abandoned and direct cyanidation practiced. The precipitation practice finally evolved for the cyanide solution was to use four of the boxes in pairs of two aranged in tandem, the solution issuing from the first set of boxes passing through the second set. As at San Sebastian, electrolytic precipitation was followed by zinc shaving. The zinc box was improvised by placing screens in the bottoms of a number of the compartments of two of the discarded electrolytic boxes.

At Minas Prietas the method of handling the precipitate was rather crude, as a part of the cathodes and anodes had to be removed to give access to the bottom of the boxes during the "clean-up." At Virginia City this feature of the process was greatly improved by constructing the precipitating boxes with hopper bottoms. In each compartment where one of the sloping sides of the hopper joined the vertical side of the box was located a valve through which the bulk of the solution contained in the box could be drawn prior to sluicing out the precipitate. At the apex of the hopper in each compartment was located another valve through which the slime could be sluiced to a launder which conveyed it to a small concrete tank equipped with a mechanical agitator, whence it was pumped by a centrifugal pump into an ordinary distance-frame and plate type of filter press. After drying, the precipitate was sampled and shipped to the Selby Smelting Company. Later a refinery was built. The precipitate, after retorting to recover mercury, and after the addition of the proper admixture of fluxes, was melted in graphite crucibles heated in specially designed tilting furnaces. With the arrangement described above it was not necessary to disturb the anodes or cathodes when cleaning up. Each box had twelve large compartments, in which were suspended 18 peroxidized sheet-lead anodes ⅛ inch (0.32 cm.) thick, 25 inches (63 cm.) wide and 48 inches (120 cm.) long, and 18 tin-plate cathodes of the same size. Sheet aluminum cathodes were also tried. Later, an anode composed of lead rods, detail drawing of which is shown in Fig. 7, was used. The advantage of this anode was that it could be made locally from scrap lead or old anodes. Two Wood

dynamos, each giving 500 amperes at 50 volts, and direct connected to an induction motor, furnished the current.

The character of the ore treated at this plant varied greatly. Originally it was built to treat a large accumulation of tailing which had resulted from the treatment of Comstock ores by pan-amalgamation. Later Comstock ore and concentrator tailing, and ore from the Tonopah district of Nevada, were treated. The treatment of outside ore began before the exhaustion of the tailing, so that at times there was a varying mixture of tailing and ore treated. The pan-amalgamation tailing had been retreated a number of times by the same process and was, therefore, very low grade. It contained copper, mercury, and chlorides as a result of the chemicals added during pan-amalgamation. The tonnage and metal content of the solution varied considerably, but the following is an average of the results obtained over a considerable period when treating pan-amalgamation tailing exclusively, and precipitating 474 to 668 tons of solution daily. There was no distinction made between the solution originating from the sand and slime treatment, the two being combined for precipitation. The average content of the head solution per ton was: gold 0.033 oz. (1.03 g.); silver 0.78 oz. (24.3 g.); no record of copper determinations; cyanide 0.046 percent; protective alkali 6 points. The tail solution from the electrolytic box contained: gold 0.01 oz. (0.31 g.); silver 0.22 oz. (6.8 g.); cyanide 0.066 percent; protective alkali 4 points. The zinc-box tails contained: gold 0.003 oz. (0.09 g.); silver 0.03 oz. (0.93 g.). The current density was 0.245 ampere per square foot (2.7 per sq. m.) of anode surface. The voltage across the anodes and cathodes in each compartment was 3.1. The average content of the head solution when treating a mixture of Tonopah ore and pan-amalgamation tailing was: gold 0.055 oz. (1.71 g.); silver 3.15 oz. (98.0 g.); cyanide 0.18 percent; protective alkali 10 points. The tail solution from the electrolytic boxes, when precipitating 432 tons per 24 hours, contained: gold 0.02 oz. (0.62 g.); silver 0.60 oz. (18.7 g.); cyanide 0.18 percent; protective alkali 10 points. The current density was 0.245 ampere per square foot (2.7 per sq. m.) of anode surface. The voltage

across the anodes and cathodes in each compartment was between 3.1 and 3.2. Four lots of precipitate contained the following percentages of gold, silver, and copper:

TABLE I.

	Percent		
	Gold	Silver	Copper
A	0.23	9.60	26.60
B	0.23	8.49	29.25
C	0.29	9.99	31.40
D	0.27	7.97	20.10

Table II shows the results obtained in one of the boxes when the conditions of tonnage precipitated, current density, voltage, etc., were the same as those given above.

TABLE II.

(Multiply figures by 34.29 to get grams per metric ton)

	Assay of Solution		Amount Precipitated	
	Silver, Oz.	Gold, Oz.	Silver, Oz.	Gold, Oz.
Solution entering electrolytic box	2.164	0.0403	....	....
Solution leaving:				
1st compartment	2.049	0.0405	0.115	0.0
2d "	1.756	0.0335	0.293	0.068
3d "	1.751	0.0335	0.005	0.0
4th "	1.669	0.0310	0.082	0.0025
5th "	1.418	0.0265	0.251	0.0045
6th "	1.427	0.0275	0.0	0.0
7th "	1.271	0.0240	0.156	0.0035
8th "	1.193	0.0215	0.078	0.0025
9th "	1.124	0.0205	0.069	0.0010
10th "	1.022	0.0175	0.102	0.0030
11th "	0.886	0.0140	0.136	0.0035
12th "	0.824	0.0105	0.062	0.0035
Solution leaving:				
1st Zinc	0.417	0.0075	0.407	0.0030
2d "	0.225	0.0045	0.192	0.0030
3d "	0.048	0.0015	0.177	0.0030

Table III shows the composition in gold and silver deposit, as determined by corrected assay of the cathode deposits in the various compartments of the precipitation equipment when treating exclusively Tonopah ore. In the case of the electrolytic box, each sample was taken directly from the surface of the cathode.

TABLE III.

	Percentage, Silver	Percentage, Gold	Percentage Base Metals and Other Impurities, by Difference
1st Electrolytic Compartment....	87.69	1.98	10.33
2d " "	88.38	1.98	9.64
3d " "	80.02	1.82	18.16
4th " "	81.43	1.89	16.68
5th " "	77.95	1.77	20.28
6th " "	77.50	1.81	20.69
7th " "	67.09	1.48	31.43
8th " "	69.71	1.58	28.71
9th " "	58.33	1.37	40.30
10th " "	62.39	1.41	36.20
11th " "	55.72	1.25	43.03
12th " "	49.96	1.12	48.92
1st Zinc Compartment.....	59.38	1.37	39.25
2d " "	46.20	1.03	52.77

PRACTICE AT EL RAYO, MEXICO.

The equipment installed at El Rayo followed rather closely the lines of that used at San Sebastian, Salvador, and consisted of one wooden box 10 feet (3 m.) wide by 20 feet (6 m.) long, 4 feet (1.2 m.) deep on one side and 5 feet (1.5 m.) deep on the other, with the usual arrangement of wide and narrow compartments. In each of the seven wide compartments were installed 25 sheet-lead anodes, 20 inches (50 cm.) by 40 inches (100 cm.) and ⅛ inch (0.37 cm.) thick. Alternating with the sheet-lead anodes, there were 24 sheet-copper cathodes, 20 inches (50 cm.) by 40 inches (100 cm.) and 1/32 inch (0.08 cm.) thick. Electrical connection of the anodes and cathodes to the bus bars was made by means of lead plugs cast onto the plates, to which were soldered copper connecting wires. The current was supplied by a Crocker-Wheeler generator giving 500 amperes at 50 volts.

At the time that this installation was made, zinc-dust precipitation of the gold and silver was giving satisfactory results. A change in the character of the ore indicated that trouble might arise through a greatly increased proportion of copper. It was, therefore, planned to continue to precipitate the gold and silver by zinc and depend upon electrolytic precipitation to keep the copper in solution down to a concentration which would not

interfere with cyanide treatment. To this end 200 tons of solution, the total flow from the zinc precipitation equipment, was passed through the one electrolytic unit. The intention was to deposit the copper in as pure a state as possible so that it could be marketed directly. Certain difficulties arose in accomplishing this end, and before they were overcome, the proportion of copper in the ore had decreased to a point where it was no longer necessary to use electrolytic precipitation.

The equipment was not dismantled and stood as originally installed until the exigencies of the Mexican revolution caused the management to turn to it in an effort to conserve both cyanide and zinc. In this case the original practice was reversed. The cyanide solution was passed directly from the treatment tanks to the electrolytic precipitation box and from thence to the zinc-dust precipitation equipment. There was an average of 200 tons per day of solution precipitated. The average content of this solution was as follows:

Simple alkaline cyanide	0.15 percent
Total cyanide	0.38 percent
Alkalinity	100 points
Copper	0.12 percent
Zinc	0.05 percent
Gold	0.30 oz. (9.3 g) per ton
Silver	5.00 oz. (155.5 g) per ton

Approximately 65 percent of the gold and silver, 20 percent of the copper, and a small amount of zinc were precipitated by electrolysis. There was a gain in cyanide strength of about 0.075 percent, with a considerable decrease in the alkalinity. The current density used was 1.2 amperes per square foot (13.2 per sq. m.) of anode surface. Under these conditions of operation the lead anodes disintegrated very rapidly.

PRACTICE AT NELSON, BRITISH COLUMBIA.

In 1907, Douglas Lay described a modified Siemens-Halske installation in use at the Reliance mill, Nelson, British Columbia. The three wooden containing tanks were 35 feet (10.5 m.) long, 5 feet (1.5 m.) wide, and 3 feet (0.9 m.) deep, inside dimensions. The anodes were No. 10 sheet iron (0.35 cm. thick), 5 ft. 1 in. (153 cm.) by 2 ft. 8 in. (80 cm.), set in saw cuts three inches (7.5 cm.) apart, made in the sides and bottom of the con-

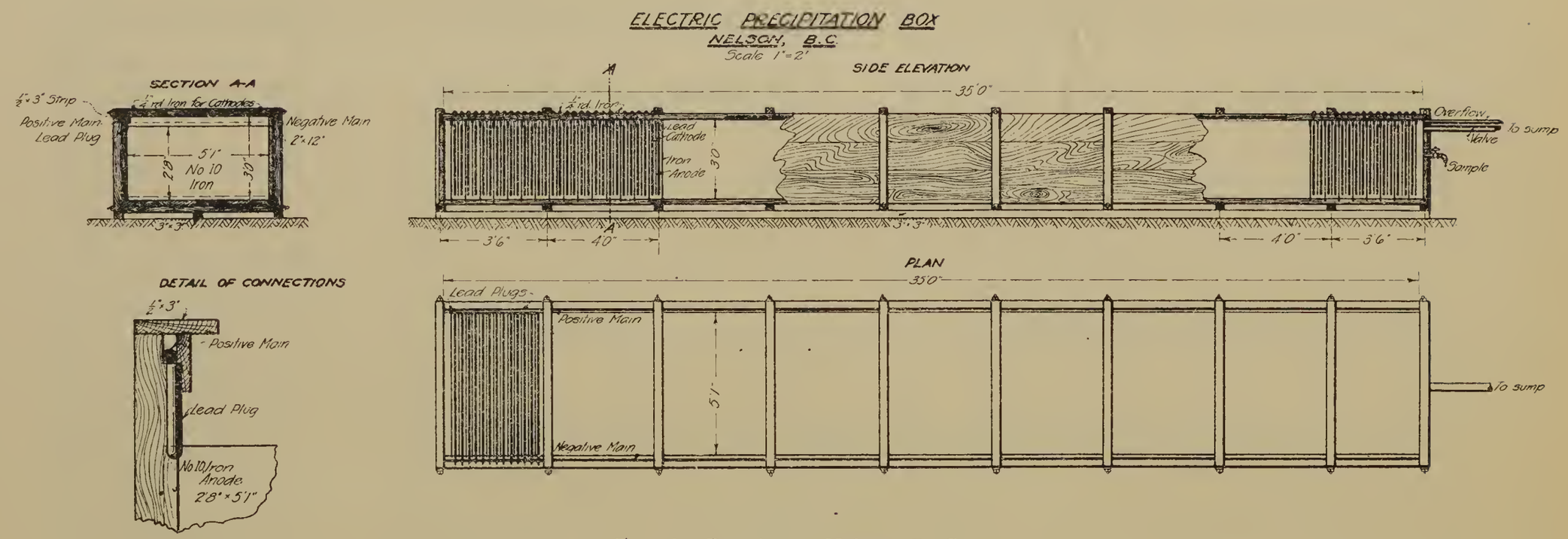


Fig. 6. Practice at Nelson, B. C.

taining tank. The alternate downward and upward flow of the solution, by which means it was caused to pass uniformly by the anode and cathode surfaces, was attained by setting each alternate anode 1½ inches (4 cm.) off the bottom of the box, the solution passing under these anodes and over those set into the bottom of the box. The anodes were enclosed in cheesecloth to prevent short circuiting. Connections to the main positive wire, which rested in a groove in the top of one side of the box, were made by means of lead plugs cast in holes bored downward to intersect the top edge of the anodes where they rested in the saw cuts in the side of the box. The cathodes were sheet lead about 1/40 inch (0.6 mm.) thick, made by a special casting process at the Trail smelter, and of approximately the same area as the anodes. For convenience in handling, each cathode was made up of three sheets, each weighing about 7 pounds (3 kg.), attached to a ¼-inch (0.6 cm.) round iron cross-bar by two strips of roofing tin.

The cathodes previous to being used were dipped momentarily in a slightly acidic solution of zinc chloride to clean them thoroughly. Connection of the cathodes to the main negative wire, which rested on top of the opposite side of the box from the positive main, was made by direct contact of the cross-bar at one end with the negative wire upon which it rested. The other end of the cross-bar rested upon a strip of wood which insulated it from the positive main. The distance between the anodes and cathodes was therefore 1½ inches (4 cm.). Each box contained approximately a total of 3,500 square feet (320 sq. m.) each of anode and cathode surface. A detailed drawing of the whole arrangement is shown in Fig. 6. The three boxes precipitated 150 tons of solution per 24 hours, resulting from the treatment of 50 tons per day of low-grade gold ore containing 0.20 oz. (6.2 g.) gold ($4.00) per ton. The solutions precipitated were kept at 70° F. (21° C.). A low current density of 0.02 to 0.03 ampere per square foot (0.22 to 0.33 per sq. m.) of cathode surface was used. The voltage across the anodes and cathodes was 4 to 5. Accurate figures are not available for the composition of the head solution precipitated, but the following are reasonably accurate estimates: Gold 0.06 oz. (1.75 g.) ($1.20) per ton; cyanide 0.01 to 0.05 percent, and pro-

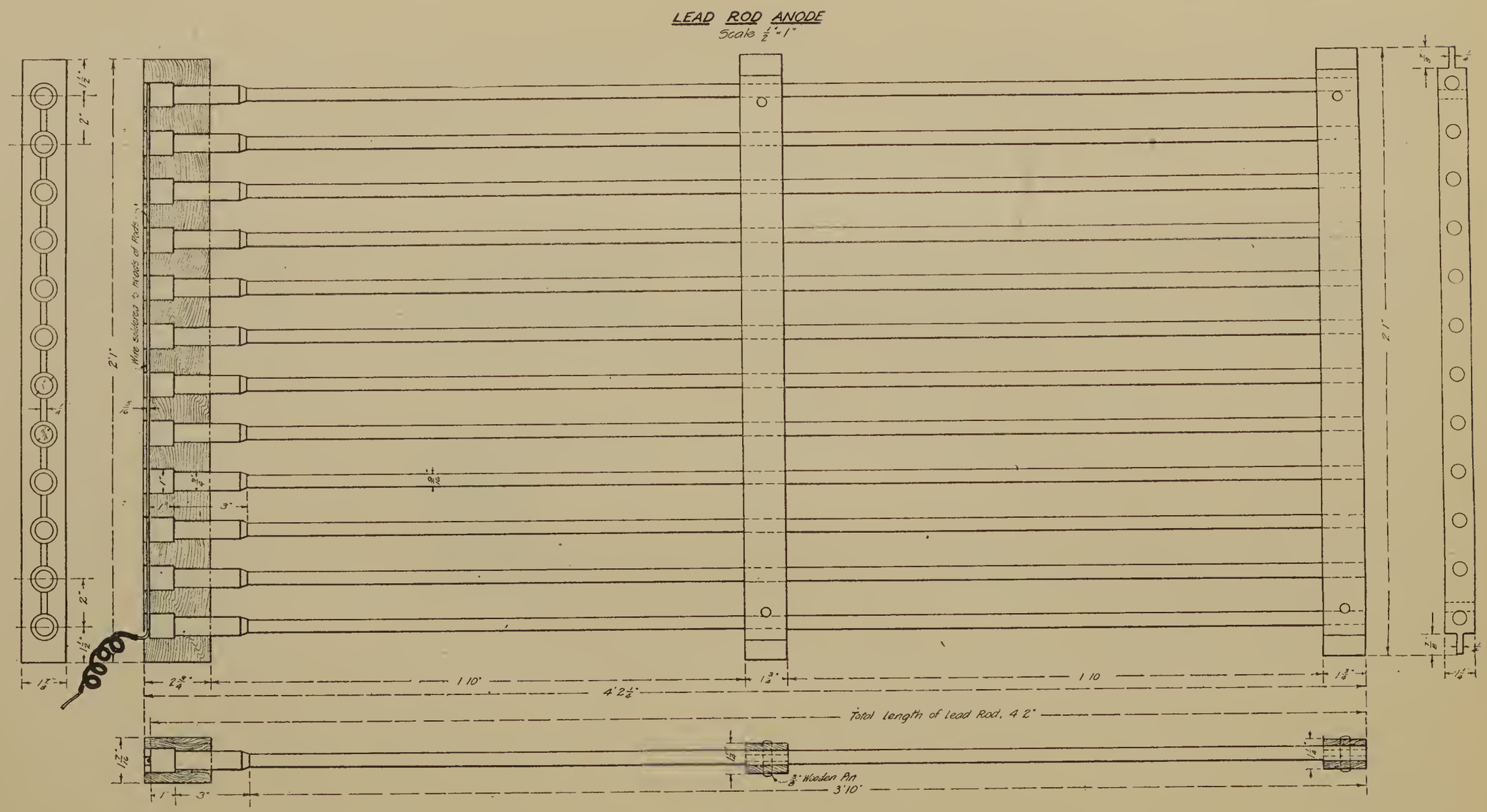

LEAD ROD ANODE
Scale 1/2" = 1"
Wire soldered to heads of Rods
2'1"
1 10"
4'2 1/4"
Total length of lead Rod, 4 2"
3/8" Wooden Pin
3'10"

FIG. 7.

tective alkalinity twenty-three points. The tail solution contained from a trace to a few cents in gold per ton. When protective alkali was present there was no loss of cyanide in passing through the precipitation box, but when there was no protective alkali about 30 percent of the cyanide was decomposed by the current. Presence of sufficient alkali also caused the iron dissolved at the anode to separate as ferric hydroxide, instead of the prussian blue formed when there is insufficient alkali. In this installation a special arrangement was made to run off the ferric hydroxide which collected on the surface of the solution, by shutting off the regular outflow and allowing the solution to rise above the tops of the high anodes and overflow momentarily from an auxiliary outflow carrying with it the ferric hydroxide. This operation required but two or three minutes upon each shift.

ANODES.

Iron anodes were used with the Siemens-Halske process in South Africa, but lead, with a few exceptions, has been used in American practice. Various other anode materials have been tried but, everything considered, lead is the most satisfactory. One important advantage that lead has over many other anode materials is that it has a certain salvage value after it has served its useful life as an anode. It has been used both plain and peroxidized, but in general the peroxidized anodes have had the longest life. Many investigators have reported certain anodes as being satisfactory when used in cyanide solutions, but these tests carried on in a small way have always covered entirely too short a period of time. The fact that an anode will stand up for two or three days of continuous operation in no way signifies that it will be satisfactory for a period of operation sufficiently long to make its use commercially economical. Experiments with Acheson graphite have been most disappointing, notwithstanding the favorable reports made by other investigators who have tried out this material in a small way for short periods of time. The graphite anodes gradually become mushy and soft, and finally are useless. The reason for the failure of the graphite anode is not clear, but at one time I thought that it was due to the disintegration of the binding material used in the original carbon plates from which the graphite plates were

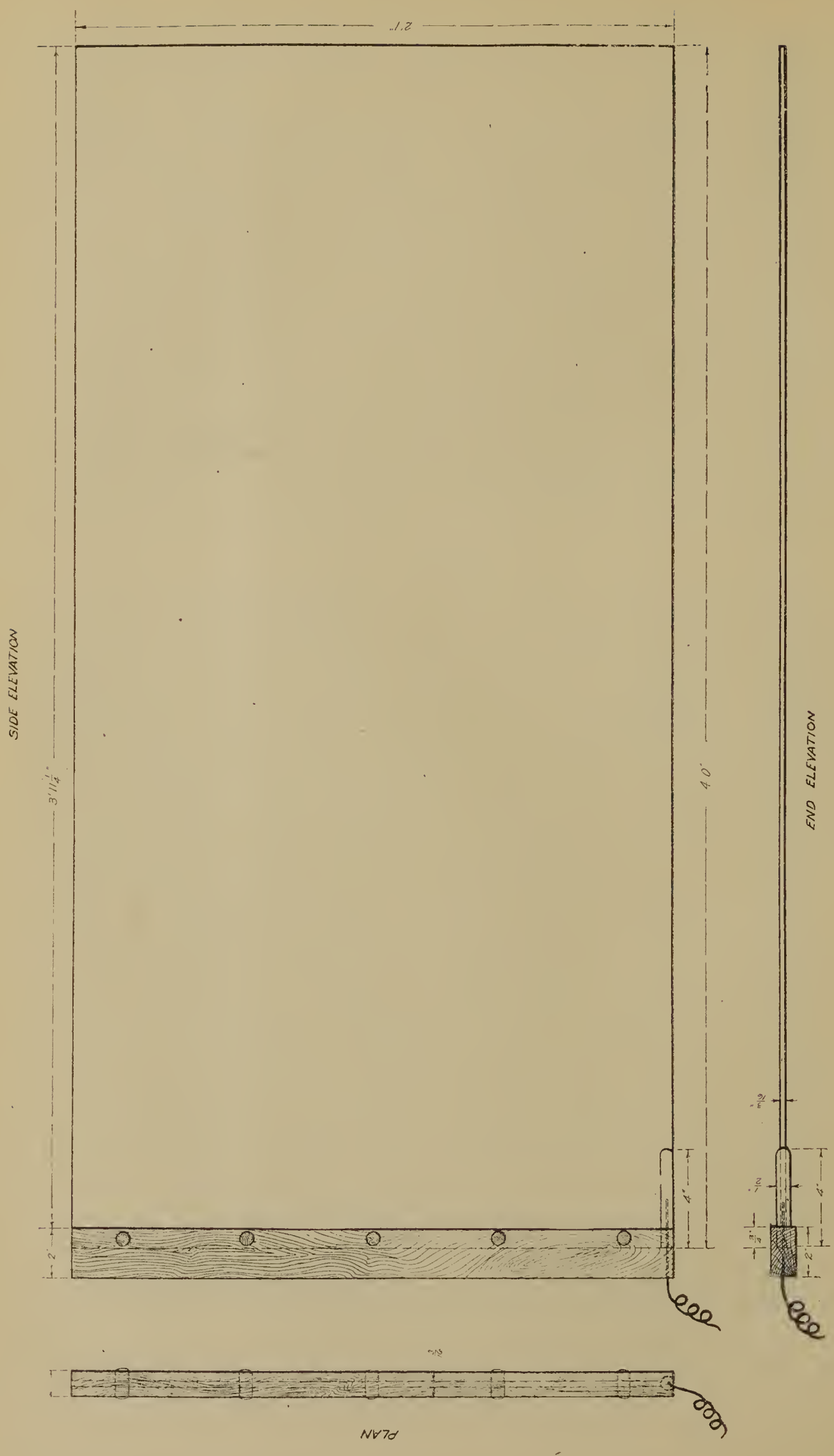
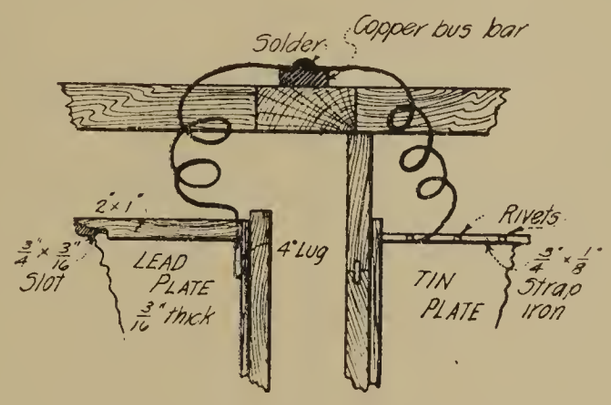


Fig. 8. Lead Plate Anode.

made. In other words, the graphite resulting from the carbonaceous binding material of the original carbon plate does not appear to form a strong union with that resulting from the carbon proper of the plate.

The sheet-lead anodes are made up as shown in Fig. 8. The sheets of lead, after cutting to the desired size, are thoroughly cleaned and in one corner or on the two opposite corners of the short dimension of the sheet is cast a special connecting lug, ½ inch (1.3 cm.) in diameter by 4 inches (10 cm.) long, by means of a special iron mould which firmly clasps the plate at the point where the lug is to be attached. The lugs are cast from lead to which has been added a small amount of tin, to lower its melting point. The temperature of the lead used in



Detail of Connections (see Fig. 8).

casting the lug should be such that does not melt through the lead sheet, but still is sufficiently hot to form a thorough union with the lead sheet. A tongued wooden supporting strip is attached to the top of the plate by means of wooden pins.

The lead-rod anodes are made up as shown in Fig. 7. Lead rods of the form shown in the drawing are cast in special iron moulds, observing the usual precautions for preventing the oxidation of lead during melting and the obtaining of a clean, smooth casting free from holes or spongy spots. Twelve of these rods supported in strips of pine drilled to receive them at the bottom, at the center and at the top, comprise an anode. The bottom and center strips are 1.75 in. (4.4 cm.) by 1.25 in. (3.2 cm.), and are kept from shifting by means of wooden pins which engage

the two outside rods. These also serve to prevent short-circuiting of the tin-plate cathodes, which have a strong tendency to buckle. The top strip, 2¾ x 1⅞ inches (7 x 4.7 cm.), is counterbored to receive the large ends of the rods and supports the whole weight of the anode. Electrical connection to the individual rods is made by soldering to them a No. 10 (2.5 mm. diameter) copper wire, which rests in a groove at the top of the strip. The continuation of this wire serves as the means of connecting the anode to the bus-bar.

The method of peroxidizing the anodes varied somewhat at the different plants. This operation was performed in a separate cell where a few anodes at a time were treated. The first step was to clean and brighten thoroughly the surface of the lead with a scratch brush. At Minas Prietas a 1 percent potassium permanganate solution was used and a current density of 1 ampere per square foot (11 per sq. m.). The time was one hour or longer. During the operation the strength of the solution was frequently tested with a standard solution of ferrous sulphate, fresh permanganate being added to keep the solution as near 1 percent as possible. At San Sebastian various combinations were tried, but the practice that met with the most favor was to use an electrolyte containing 1 percent of potassium permanganate, 2 percent of sulphuric acid and a current density of 2½ amperes per square foot (27.5 per sq. m.). The time of treatment was 6 hours. In passing, it is well to mention that it has been found in certain of the electrochemical industries that a denser and more satisfactory coating of the peroxide is formed if the operation is performed in an alkaline solution.

At Virginia City the peroxidized lead anodes had a life of about one year. At San Sebastian, on account of the higher current density the life was 8 to 12 months. At Minas Prietas the life was in some cases considerably over a year.

CATHODES.

The lead-plate cathodes used at San Sebastian were constructed similar to the anodes, except that the sheet lead used was thinner.

An interesting feature of the lead cathodes used at the Reliance mill was that they were not ordinary rolled sheet lead, as had been previously used elsewhere for both anodes and cathodes,

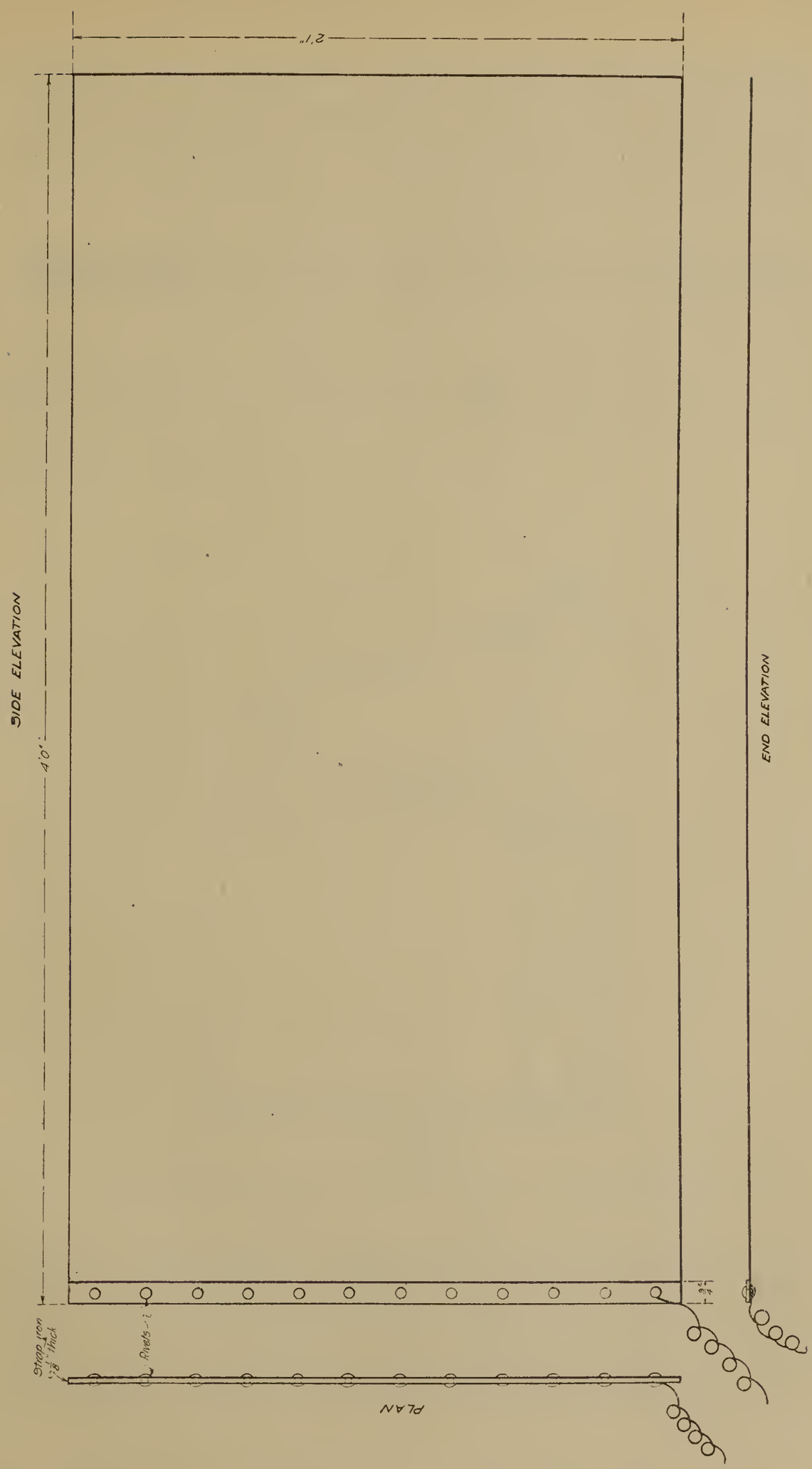


FIG. 9. Tin Plate Cathode.

but plates cast upon an inclined plate machine at the Trail smelter. The simplicity of the arrangement will be apparent from the drawing shown in Fig. 11. It was said that one man could make 500 cathodes in a shift.

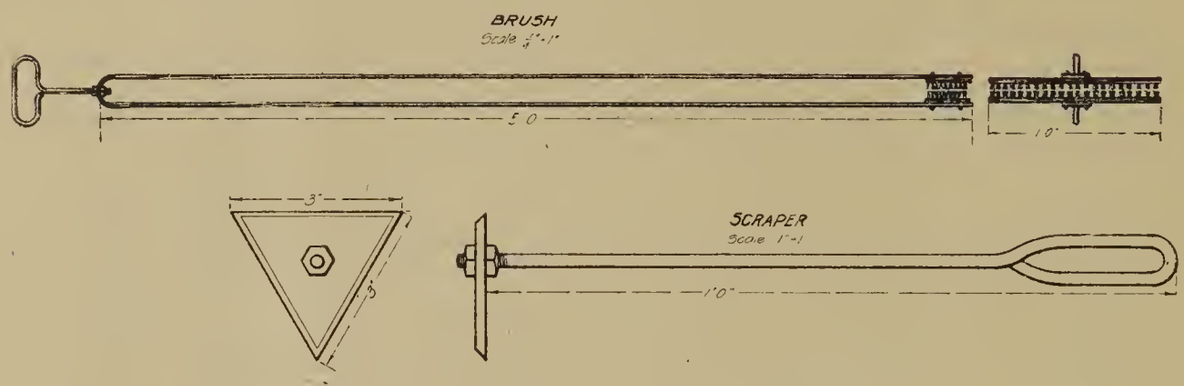


FIG. 10. Tools for Cleaning Cathodes.

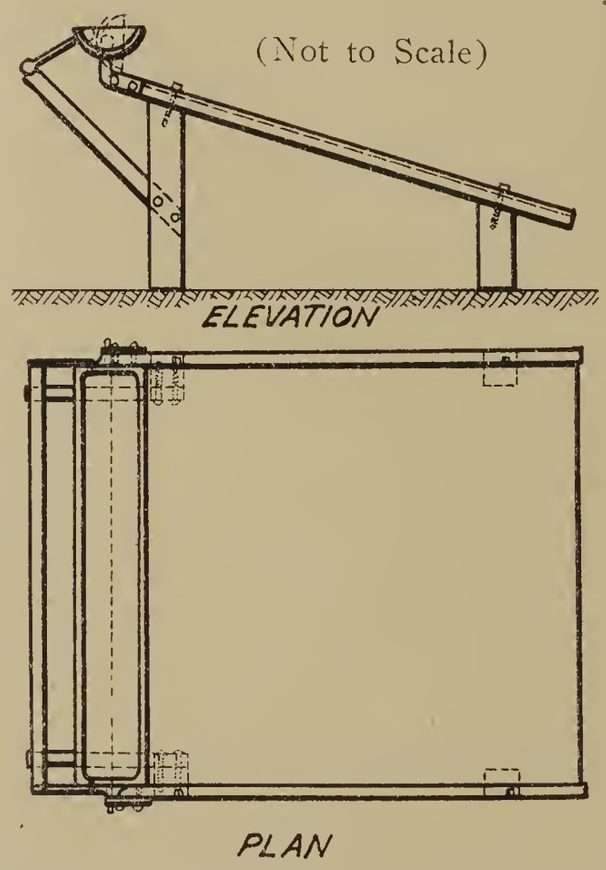


FIG. 11. Casting Machine for Lead Plate Cathodes, Trail Smelter, B. C.

The tin-plate cathode was made from medium-weight tin-plate, as shown in detail in Fig. 9. A piece of strap iron ¾ x ⅛ inch (1.9 x 0.3 cm.), whose length was the same as the width of the plate, was riveted to the top. The connecting wire was introduced between the plate and strap iron in such a manner that

one of the rivets clamped it firmly in place. Fig. 10 shows the tools used in removing the portion of the deposited metals which adhered to the cathodes. The double brush was used at intervals for removing the slightly adherent deposit. The manner of using was to set it over the cathode so that a brush was bearing on either side of the cathode, when the whole tool was pressed downward until the brushes had reached the bottom of the plate; this operation was repeated until the whole surface of the plate had been covered. When it was desired to make a complete clean-up, especially if the plates were old, it was necessary to remove them entirely from the box and scrape them with the triangular scraper, shown in Fig. 10.

BY-PRODUCTS OF ELECTROLYTIC PRECIPITATION.

The by-products which appear to be inevitably produced during electrolytic precipitation and which are particularly troublesome when treating gold ores on account of the greater value of the metal involved, have always formed a most serious problem.

In the Siemens-Halske process, the Prussian blue, formed as a result of the attack on the iron anodes, had to be subjected to special treatment for the recovery of the cyanide and gold which it contained. The disadvantages arising through the separation of calcium salts, which deposited upon the anodes and cathodes and in the bottom of the box, was early noted in the application of the process. It has been variously estimated that from 0.6 to 25 percent of the gold had to be recovered from the by-products in the Siemens-Halske process.

At Minas Prietas, the precipitation of calcium salts was especially troublesome, and owing to the method of operating in which the non-coherent deposit of the metals was collected in the bottoms of the boxes, all of this eventually became intermingled with the precipitate. At this time the calcium salts, chiefly the carbonate, formed a large proportion of the precipitate. This made the precipitate more difficult and costly to smelt. Below is given a typical analysis of the lime deposit at the plant.

	Percent
Moisture	0.275
Loss upon ignition	6.060
Calcium oxide	41.580
Carbonic acid	31.120
Lead metallic	13.530
Iron oxide	0.540
Copper metallic	0.750
Sulphuric acid	4.400
Chlorine	0.670
Vanadium	0.095
Silver	0.126
Gold	0.003
	99.149

Lowered current density lessens the formation of the lime precipitate. In the course of time the lead anodes disintegrated to the extent that they had to be discarded. At first these were shipped to lead smelters, but later they were resmelted locally, and after the separation of the dross, which had to be shipped to the smelter, were cast into slabs which were rolled by a special set of rolls into sheets which were used in making new anodes.

At San Sebastian, where the gold and copper formed a coherent deposit upon the cathodes, it was possible to keep the deposit which accumulated at the bottom of the box separate from the deposited metals. However, the gold contained in this material was considerable, and at one time, when a considerable amount of it had been allowed to accumulate, it represented a great deal of value. The material more directly resulting from the disintegration of the anodes contained:

Lead	53.7 to 57.1 percent
Copper	3.1 to 4.7 "
Gold	0.031 to 0.154 "

The fine material, or "lime" as it was termed, contained:

Silica	8 to 10 percent
Alumina	22 to 28 "
Calcium oxide	15 to 21 "
Lead	Not determined
Copper	5.9 to 6.9 percent
Gold	0.322 to 0.363 "

A small blast furnace and other refining equipment was installed for treating the by-products, but on account of the high cost of coke and other supplies and the lack of skilled labor, it was generally found more economical to ship this material to smelters in the United States. No attempt was made at this plant to reclaim the anodes.

At Virginia City the conditions were much the same as at Minas Prietas. A much lower grade precipitate was invariably obtained from the electrolytic boxes than from the zinc boxes on account of the calcium precipitate. At one time, as the result of careful sampling and assaying, it was estimated that the anodes contained about 10,000 ounces of silver. This came about by reason of the fact that the solutions contained chlorine. The source of this in the tailing was the salt which had been added during pan-amalgamation and, in the Tonopah ore, was due to the occurrence of part of the silver as chloride. The presence of the silver as chloride in the anodes was proved by solution in ammonia and the regular qualitative tests. In the earlier operation the disintegrated anodes were shipped to the smelter; but later it was found that by careful heating in suitable pots the greater part of the metallic lead could be liquated, leaving most of the gold and silver in the dross. The dross was shipped to the smelter and the lead cast into rods which were mounted in wooden supports and used as anodes.

COST OF INSTALLATION AND OPERATION OF ELECTROLYTIC PRECIPITATION PLANTS.

The cost of the six electrolytic precipitation boxes at Minas Prietas, Mex., was as follows:

Box construction	$10,000.00
Dynamos	3,000.00
Lead anodes	4,455.00
Tin plate cathodes	300.00
Wiring, switchboards and instruments	1,000.00
Labor	1,000.00
Incidentals	250.00
Total for six boxes	$20,005.00

At Virginia City, Nev., U. S. A., the cost of six standard boxes was as follows:

Box construction	$6,000.00
Dynamos	4,075.00
Lead anodes	4,080.00
Aluminum cathodes	*1,598.00
Wiring, switchboards and instruments	1,000.00
Labor	1,500.00
Incidentals	250.00
Total for six boxes	$18,503.00

* N. B.—Tin plate cathodes also used.

W. H. Wood, in 1899, compiled the following comparative figures of the cost of installation on the Rand, South Africa, of precipitation equipment for operating the Siemens-Halske electrolytic and the zinc-shaving lead-couple processes for a plant crushing 500 tons of ore per day:

	Zinc-Lead Precipitation	Electrolytic Precipitation
Extractor house space	$792.18	$2,551.50
Concrete floor	296.46	928.26
Wooden containing boxes	558.90	3,159.00
Platforms	.....	703.00
Piping	109.35	257.58
Zinc (Cut.)?	299.62	.....
Dynamo	.....	1,083.78
Lead cathodes	.....	414.32
Frames for cathodes	.....	218.70
Iron anodes	.....	1,603.80
Anode bags	.....	148.23
Wiring and proportion of power	.....	1,044.90
Proportion of general charges	71.93	424.04
	$2,128.44	$12,537.11

The only costs available for electrolytic precipitation are those given below, which are the average for six years' operation of the Minas Prietas plant.

Power	$0.083
Labor	.037
Supplies	.031
Depreciation	.040
Total per ton of ore	$0.191

It will be noted that both the cost of installation and operation of electrolytic precipitation is higher than zinc precipitation.

ACKNOWLEDGMENT.

In the preparation of this paper I am indebted to the following gentlemen: Mr. Chas. Butters for information upon electrolytic precipitation obtained through visits to his plants during the time that they were in operation, as well as through personal communications; E. M. Hamilton for information contained in his paper upon the practice at Minas Prietas, also personal communications; Chas. P. Richmond for information contained in his paper upon the practice at San Sebastian, also personal communications; James Colbath for the details of the El Rayo practice; Richard Snell, H. Bulmer, and Robert Wisnom for certain

details of Virginia City practice; Douglas Lay for information contained in his paper upon the practice at the Reliance mill; and M. F. Perry for the detailed costs of installation and operation of the Minas Prietas plant. I have freely used the information contained in von Gernet's first paper upon the Siemens-Halske process, as well as that contained in other papers upon the subject which have been published at various times in the Proceedings of the Chemical and Metallurgical Society of South Africa. I also wish to acknowledge the faithful and painstaking work of my assistant, Mr. K. Pyle, in the preparation of the drawings.

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DISCUSSION.

L. H. Duschak: The cyanide solutions met with in practice, containing, as they do, very small quantities of precious metals, are very different from many solutions encountered in industrial work and comparatively little seems to be known of the exact nature of the reactions occurring in them. A good deal has been said recently about the necessity of closer co-operation between the Universities and the Industries, and it seems to me that this field offers a particularly good opportunity to the University man to lead the way. A proper understanding of the constitution of these solutions and of the chemical changes involved in the solution and precipitation of the gold and silver would in all probability aid materially in the practical development of the cyanide process.

Secretary J. W. Richards: In line with what Mr. Duschak has said, gold cannot be taken out of the solution any faster than it can get to the cathode. As a result, the efficiency, reckoned by Faraday's law, is extremely low. The ampere efficiency of deposition of the gold is probably less than one percent. That requires a very large plant, and a very large surface of electrodes. I think it is altogether within the bounds of possibility to say that by utilizing some method of bringing the solution rapidly to the cathode a higher current density and higher deposition efficiency, in a very much smaller plant, could be attained. That is one of the developments of the electrolytic laboratory, depositing with greater density, with rapid agitation, either revolving the anode or cathode, or a rapid agitation of the solution. I think it is possible to improve the process by applying these laboratory methods.

C. J. Reed: It seems to me that is the keynote of the whole difficulty, and the thing that makes electrolytic precipitation practically impossible. We have an exceedingly dilute solution, every particle of which must be brought in contact with the surface of a solid. It is so much easier to get contact with the surface of a minutely divided solid than with an electrode, because the electrode must be electrically connected and a minutely divided solid can not easily make good electrical connection. That is where the great difficulty comes in, and that is why it seems to me almost

hopeless to think of getting an electrolytic method that can ever compete with the chemical method.

Mr. Clevenger: The estimate of current efficiency given by Professor Richards is only true of certain cases and where gold is the only metal precipitated. When the weight of metal deposited is augmented by the presence of either silver or copper or both, the current efficiency becomes much greater. The current efficiencies shown in the following table have been calculated from reliable data which have come into my hands from various sources:

Name of Plant and Locality	System	Metals in Solution Precipitated	Percentage Current Efficiency
Von Gernet's General Data.....	Siemens-Halske	Gold	0.74 to 1.48
Croesus, Rand, S. Africa.....	"	"	0.29
May Consolidated (Sand) Rand, S. Africa	"	"	2.03
May Consolidated (Slime) Rand, S. Africa	"	"	0.37
Lancaster West, Rand, S. Africa.	"	"	1.10
Ferreira Slime, Rand, S. Africa..	"	"	
Minas Prietas (Sand) Mexico...	Butters-Andreoli	(a)	7.01 to 16.48
Minas Prietas (Slime) Mexico...	"	(a)	7.01 to 16.48
San Sebastian, Salvador	"	(b)	12.47 & 18.93
Virginia City, Nevada (Comstock Tailing)	"	(c)	27.15 to 38.26
Virginia City (Comstock Tailing and Tonopah Ore)	"	(c)	
El Rayo, Mexico	"	(c)	77.95
Reliance Mill, Nelson, B. C.....	Siemens-Halske	Gold	0.45 to 0.68

(a) Gold, silver and copper.
(b) Gold, copper and likely zinc.
(c) Gold, silver, copper and likely zinc.

The very high current efficiency noted in the case of El Rayo is open to question, but attention is called to the fact that complete precipitation was not attempted, and a comparatively large volume of solution was passed through a single box at a high velocity. Although certain of these results are higher than has generally been supposed to be possible in practice, yet there appears to be abundant opportunity for improvement. Some time ago the writer carried on large-scale experimental work along the lines of bringing the solution in more intimate contact with

the electrodes through agitation. This work demonstrated that the efficiency of the operation could be greatly increased by making provision for suitable agitation of the solution during precipitation. This becomes more and more apparent as the solution becomes impoverished of metal.

While the prevailing high prices of zinc and aluminum are the chief incentive at the present time for developing electrolytic precipitation, yet I am hopeful that even with normal prices of these metals it will be possible for improved systems of electrolytic precipitation, in certain cases at least, to successfully compete with them for precipitating gold and silver from cyanide solutions.

It has been suggested that a much higher current density is possible when the solution is properly agitated but, unfortunately, there are other limitations placed upon the current density which it is feasible to use. As has been pointed out in my paper, the solutions generally precipitated are poor electrical conductors, on account of the small amount of dissolved salts which they contain. Further, it is impossible to space the anodes and cathodes much closer than one and a half inches (4 cm.). Under these circumstances, a very high current density would mean a voltage which would not be practicable.

I am unwilling to agree with Mr. Reed's pessimistic views regarding electrolytic precipitation, even though it be true that, in the past, electrolytic precipitation has given way to chemical methods of precipitation. Zinc only slightly precipitates copper from cyanide solutions and I am credibly informed that it is scarcely at all precipitated by aluminum powder, two of the more commonly used chemical precipitants and both powerful reducing agents. Since copper is not precipitated by the ordinary methods of precipitation, the tendency is for it to gradually accumulate in the cyanide solution until it finally reaches a point where it occasions trouble. In the case of ores containing soluble copper compounds in appreciable amount, the only alternative seems to be electrolytic precipitation. Aside from cases where copper has to be dealt with, electrolytic precipitation presents the advantage of maintaining the solution at its highest extractive efficiency, through decomposition of deleterious compounds taken into solution, as well as through the avoidance of the addition of chem-

ical precipitants. On the whole, I am of the opinion that the electrolytic method of precipitation, through proper investigation, might be developed to the point where it perhaps could be used in conjunction with zinc or aluminum precipitation, to advantage if not entirely superseding them.

Mr. Reed: I did not make myself entirely clear. I referred only to very dilute solutions. I had in mind only gold and silver. Where copper comes in to interfere it is generally in a relatively larger proportion. My remarks would not apply to that.

Mr. Clevenger: Copper does not need to be present in an ore, in a relatively large amount to seriously interfere with cyanidation, for the reason, previously explained, that a small amount of copper dissolved from each successive charge of ore may concentrate in the solution until a point is reached where it may cause serious interference. For example, at Minas Prietas the weight of silver dissolved was twice that of the copper.

Mr. Reed: To what extent would that copper increase? What relative proportion?

Mr. Clevenger: I have never ascertained the maximum concentration which copper would reach in the ordinary mill solution, but a case which I might cite as illustrative of the concentration where trouble begins to be apparent with the extraction of the gold arose in connection with the treatment of the gold ores from the San Sebastian mine, San Salvador, Central America. With a relatively higher concentration of cyanide in solution than generally used in the treatment of gold ores, when the copper reached a concentration of 0.2 percent the interference with extraction began to become apparent. This happened when there was a greater proportion of soluble copper in the ore treated than the electrolytic equipment was capable of precipitating. When the copper in solution was reduced through electrolytic precipitation, the extraction again became normal.

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SINGLE POTENTIALS IN THE SILVER CYANIDE PLATING BATH, AS AFFECTED BY ITS COMPOSITION AND CONCENTRATION.

By Francis C. Frary and Ralph E. Porter.

THE INFLUENCE OF FREE CYANIDE, CHLORIDE AND HYDROXIDE.

The work herein described was begun two years ago as a part of the work of the committee appointed at the Atlantic City meeting of this Society, to co-operate with the American Electroplaters' Association. Prof. W. D. Bancroft, the chairman, divided up the field and assigned the testing of silver-plating baths to one of us, who was a member of the committee. The purpose of the work as planned was to study the effect of the various materials recommended for use in or addition to the silver-plating bath, as described in a previous paper.[1] This problem is so large, however, that it seemed best to confine the work at first to the bath in common use, silver potassium cyanide, and study the effects of various proportions of its ingredients and impurities on the character of the deposit.

It is obviously impossible in a laboratory study to duplicate the conditions of practical working, especially in respect to the continuous working of a bath day after day for months. The way which seemed most promising was to study the effect of various substances in the bath upon the single potential of some of the metals from which objects to be silver-plated are usually made, and thus determine whether the coat would be likely to be adherent or not.

It appears to be generally understood and agreed that, aside from troubles due to improper cleaning of the object, the cause of a non-adherent deposit is to be sought in the fact that some of the metal upon the surface of the object to be plated has dissolved in the bath during the operation, and thus the deposit is only loosely attached to the object. If only a thin coat is

[1] Frary, Trans. Am. Electrochem. Soc., 23, 25 (1913).

to be given, and the time of immersion is short, the coating will usually be fairly satisfactory, even though a little of the surface of the object has been dissolved, and it is upon this fact that the various dipping baths depend. But thicker coats, which must be deposited electrochemically by the use of outside sources of energy, will not generally adhere well unless deposited upon a surface which is not attacked by the bath.

An excellent illustration of this is seen in the copper-plating industry. It is known that in producing copper-plated wire, all that is necessary is to immerse the pickled wire in a strong copper sulphate solution for a very short time, and rinse, when an extremely thin coat of copper will have been deposited on the surface and will adhere tenaciously throughout the subsequent operations of drawing and annealing. On the other hand, if an iron object is to be plated with copper for any purpose where more than a few thousandths of an inch of copper is needed, it is well known that the operation cannot be started in a sulphate bath if an adherent deposit is to be obtained. A double cyanide bath is therefore used, in which the iron does not dissolve appreciably, and only after a solid coating of copper thick enough to protect the iron has been deposited can the object be transferred to the sulphate bath, in which the operation is completed. The sulphate bath is preferred on account of the fact that more copper is deposited by a given current from it than the cyanide bath, but its power of dissolving the iron renders its direct use on iron objects undesirable.

It is evident that the single potentials of the metals in a given silver-plating bath, as compared with the single potential of silver in the same bath, will tell us whether they have a tendency to dissolve at the expense of the silver in solution or not, and if they have such a tendency, its amount will be measured. In general, only such metals will dissolve appreciably in silver potassium cyanide as are less noble (more negative) than silver, and they dissolve only by replacing (and precipitating) the silver in solution. Since silver and most other metals which are soluble in potassium cyanide form complex double salts which are probably only slightly ionized, it seemed impossible to predict or calculate satisfactorily any of the data desired, so they were all directly determined.

A few measurements of the single potential of silver in solutions containing silver potassium cyanide have been previously made, but in view of the difficulty of determining the purity of the cyanide employed, and the small number of results available, they were not considered. The results used in this study must be strictly comparable with one another, in order to be of value, and the influence of unavoidable impurities was therefore minimized by using materials of the same quality and composition throughout.

MATERIALS.

Potassium Cyanide. This chemical is notorious for its varying quality, and for the difficulty found in preparing it in a pure state. Commercial (99 percent) cyanide contains, according to its makers, quantities of sodium cyanide, as well as other materials. As it appeared probable that each impurity present would affect the results, it was desired to obtain a pure cyanide. As some of Kahlbaum's C. P. cyanide was at hand, it was analyzed by titration with silver nitrate, according to Liebig[2] with the addition of a little potassium iodide solution to give a sharper end-point[3]. The analyses indicated cyanogen corresponding to only 94.6 to 94.9 percent KCN. In order to determine the impurity, a carbonate determination was made by treatment with barium nitrate in a stoppered flask. The result indicated the presence of 0.77 percent potassium carbonate. This is probably too high, as it has been pointed out by Mellor[4] that barium cyanate is also more or less completely precipitated.

The method of Paterno and Pannain[5] recently recommended by Clevenger and Hall[6] was then tried. It indicated that the total of cyanate, carbonate, hydroxide, chloride, and other salts aside from cyanide, whose acid radicals are completely precipitated by silver nitrate in neutral solution, was negligibly small. Attempts to titrate the amount of cyanide present after removing carbonate, by addition of barium nitrate and titration without filtering off the carbonate, gave slightly higher results (95.4

[2] J. Chem. Soc., **4**, 219.
[3] Deniges, Compt. rend., **117**, 1078.
[4] Z. Anal. Chem., **34**, I, 17.
[5] Gaz. Chim. Ital., **34**, II, 152.
[6] Trans. Am. Electrochem. Soc., **24**, 277 (1913).

percent). In this case the determination was made by adding an excess of standard silver nitrate solution, making up to a given volume, settling, and titrating excess silver in an aliquot portion of the clear supernatant liquid. By the same method, without addition of barium nitrate, 95.77 percent of cyanide was found. Addition of bismuth hydroxide to remove sulphides gave practically the same result as the barium nitrate; the presence of both barium nitrate and bismuth hydroxide in the solution reduced the apparent cyanide to 94.82 percent. No sulphide could be detected calorimetrically, however.

Qualitative tests for sulphuric acid gave negative results. As nothing else could be discovered in the sample, it was thought that possibly the cyanide had been hydrolyzed to formate. Two attempts to get qualitative tests for this substance by reduction with magnesium ribbon and sulphuric acid to formaldehyde, and testing for the latter according to Leach[7] gave negative results.

At our request the J. T. Baker Chemical Co. prepared a sample of "C. P." potassium cyanide for us, in the hope of getting a purer product. A cyanogen determination by Liebig's method with the addition of iodide gave 96.34 percent potassium cyanide, while Paterno and Pannain's method showed 0.065 percent of impurities precipitated by silver nitrate in neutral solution. No sulphates were present. A determination of moisture was attempted by drying two grams to a constant weight in an electric drying oven at 105° C. To prevent the absorption of carbon dioxide powdered potassium hydroxide was kept in the oven during the determination. Only 0.02 percent of loss (moisture) could be found.

As a check on the moisture determination, the amount of potassium in the salt was determined by weighing a sample into a platinum dish, evaporating with an excess of hydrochloric acid and weighing the potassium chloride after careful ignition. The weight of chloride found corresponded to a content of 99.85 percent cyanide in the original salt. No sodium was present.

It was suspected that possibly some of the hydrocyanic acid was being lost by hydrolysis and action of carbon dioxide between the weighing and titration of the sample. To prevent

[7] Food Analysis, page 180.

this a sample of about 1.2 g. was weighed from a weighing bottle directly into a potassium hydroxide solution and titrated immediately. Only 96.29 percent of cyanide was found, as against 96.34 percent in two previous determinations. Evidently this did not account for the low results.

On looking over the literature of the method, it appears that no one has ever checked it up on a salt of known purity, or been able to definitely show that it gave accurate results. Liebig himself in describing the method[8] says "Titration is very accurate for HCN, but when applied to KCN gives an unexpected result of low purity." Nevertheless this method appears to have become standard, and practically no other one has been used.

Another method has been proposed, however, by Hannay,[9] who states that potassium cyanide can be determined in cyanide solutions by titration with mercuric chloride, even though the solution may already contain AgCN. He states that the presence of HCNO, HCNS, or silver salts does not interfere with the method. The equation is given as:

$$2\ KCN + HgCl_2 = Hg(CN)_2 + 2\ KCl$$

He states that the cyanide solution must be alkaline, preferably with ammonia. As the method looked promising it was tried, and found to give higher results than the other. The mercuric chloride was made up by dissolving a quantity of the pure salt in water and dilution to definite volume. Its composition was checked gravimetrically, by precipitation as sulphide, filtration on a Gooch crucible, thorough washing first with water, then with acetone, then with carbon-disulphide to remove traces of free sulphur, then with acetone again to remove the carbon disulphide, and finally with alcohol. When dried to constant weight duplicate determinations agreed very well and checked the calculated strength within the limit of allowable error.

An analysis of the sample of Baker's C. P. cyanide by this method, using an ammoniacal solution and adding a few drops of potassium iodide as an indicator, gave the following results: On a 0.2 g. sample weighed into the ammoniacal solution and titrated with mercuric chloride: KCN = 99.59 percent. On

[8] *Loc. cit.*

[9] J. Chem. Soc., T, 245 (1878).

a five-gram sample made up to 100 cc., and 1 g. aliquots removed on successive days, titration with mercuric chloride showed 99.10 percent, 98.81 percent and 98.70 percent. It is evident that the solution was slowly hydrolyzed on standing. The 0.2 g. sample was probably too small to give a reliable result. The other two one-gram aliquots of this solution were then titrated according to Liebig's method, with KI as indicator, and gave 95.76 and 95.63 percent, as against 96.3 percent previously found on fresh samples. It is therefore evident that the mercuric chloride method gives results about 3 percent higher than the silver nitrate titration, and apparently from the other results obtained on these samples, the fault is in the silver nitrate titration. This matter will be taken up and investigated in this laboratory in the near future. We felt that this work had shown that the impurities in the samples of cyanide were practically negligible as far as their probable quantity and its effect on the work in hand were concerned, and Kahlbaum's sample was therefore used in making up the standard cyanide solutions used herein, its strength being assumed to be that shown by the highest of the titrations according to Liebig. Since this method is standard, it was thought best to accept it for the calculations, and if it should prove later that the mercuric chloride method is correct, the proportions of actual cyanide present in the solutions here used will simply have to be increased about 3 percent in the tables. These results, however, approximate as closely as may be what would be obtained by making up the solution from a sample of cyanide sold as containing a certain proportion of the salt, since this proportion would have been determined by the silver titration.

The method recently recommended by Lundell[10] was not tested, as there was no reason to believe that it would be more accurate than the method of Liebig, and the analyses given by its originator indicate that it gives slightly lower results than the latter.

Potassium Silver Cyanide. This was prepared by adding pure silver nitrate, in slight excess, to a potassium cyanide solution. The precipitated cyanide was filtered, thoroughly washed and dissolved in the smallest possible amount of a hot, strong potassium cyanide solution. Upon cooling and adding about one-

[10] Trans. Am. Electrochem Soc., **25**, 369 (1914).

third its volume of alcohol, the greater part of the salt crystallized out. It was filtered, washed with alcohol and dried. A second crop was obtained by evaporation and addition of more alcohol, and the whole redissolved in a minimum quantity of hot water. A little silver nitrate was added to produce a permanent precipitate, cyanide added to just dissolve this, and the whole was boiled and filtered. After cooling in ice-water the crystals were separated and dried as completely as possible by suction, and then spread out in a thin layer to complete the drying. A second and third crop was obtained. The salt made a clear solution in distilled water, and was analyzed. One g. of it required approximately 0.4 cc. of fifth-normal silver nitrate to produce a permanent turbidity. Subtracting this as a blank, and determining the quantity of silver required for complete precipitation, the sample appeared to contain 100.3 percent of the cyanide required to form KCN.AgCN. The trace of free cyanide evidently present appears to be necessary in order to prevent precipitation of silver cyanide, as experiments with the salt obtained by crystallization directly from the hot solution which had been digested with an excess of silver salt showed that it always gave a slightly turbid solution and left a residue of undissolved silver cyanide. This double salt was used in the work on the single potentials.

METHODS.

The potentials were measured by the potentiometer method, using a Kompensations-apparat nach Franke[11], with two cells of an Edison storage battery and an auxiliary rheostat for fine adjustment of the current. The apparatus was adjusted by using a standard cadmium cell, made in the laboratory and compared with one certified by the Reichsanstalt. The galvanometer used was of the D'Arsonval type, very sensitive, and protected by a resistance of 100,000 ohms during the rough adjustments. A normal calomel electrode was used, with a 3.5 N solution of potassium chloride as an intermediate liquid.

A thermostat was not used, as it would have complicated the work too much in proportion to its value. The temperature was taken when each determination was made, and the E. M. F. of

[11] Z. Instrumentk., 23, 93.

the calomel electrode corrected for it, according to the standard formula $E = + .560 + .0006(t-18)$. It is believed that the changes in the single potentials due to the temperature were small; and within the limits of error from other sources, notably that of precipitation of silver on the electrode in many cases. The electrodes were carefully cleaned with sandpaper just before use, and care was taken to get the reading as near the equilibrium value as possible.

The metals differed considerably in their behavior during the determinations. Silver usually came to equilibrium quickly, the values becoming progressively more negative or less positive until equilibrium was reached. Copper behaved similarly. In most cases brass was at first more negative and then rather rapidly approached the final value from the negative side. Evidently the free zinc gives the first observations, but as that is used up we approach the value for the zinc-copper alloy. Brass then really can have a considerably more negative potential than that shown in the table. Mercury and iron approached the equilibrium from the negative side, becoming progressively more positive. Iron was very slow to reach the equilibrium.

After the results had been plotted into preliminary curves, some of those figures which seemed to be out of their proper place in the curve were redetermined, until we were satisfied that the results were as nearly correct as we could obtain. Even so, we have not plotted the results obtained either with plain or amalgamated zinc, and have omitted making the determinations with these electrodes in some cases, as the precipitation of silver and the drop of the (negative) voltage were so rapid as to make the figures of little value.

Attempts to determine the hydrogen potential in the solution were unsuccessful, as the stream of gas carried away HCN on account of the hydrolysis of the KCN, and so the values changed rapidly.

For the information of the plater, the specific conductivity of the solutions was also determined and is recorded in the tables, together with the temperature at which it was determined.

The plan followed in the work was to prepare a solution of known strength and proportions of constituents, and test a part of it. The rest was then diluted with various quantities of water

TABLE I.

Single potentials of various metals in solutions of potassium silver cyanide with potassium cyanide.

RATIO	DILUTION		ELECTRODE POTENTIALS														Specific Conductivity	
	Potassium silver cyanide	Free potassium cyanide	Mercury		Silver		Copper		Brass		Iron		Zinc		Amalgamated Zinc		Temp.	Mhos
			Temp.	Volts	Temp.	Volts	Temp.	Volts	Temp.	Volts	Temp.	Volts	Temp.	Volts	Temp.	Volts		
1:0	2	none	23	+0.167	23	+0.396	23	+0.393	23	+0.388	23	+0.345	21	+0.198	22	+0.062	22.6	0.0594
	4	none	23	+0.156	23	+0.427	23	+0.421	23	+0.412	23	+0.356	21.5	+0.132	21.5	+0.002	22.7	0.0318
	8	none	23	+0.157	23	+0.460	23	+0.451	23	+0.447	23	+0.370	19	*—0.280	21.5	*+0.032	22.1	*0.0110
	16	none	23	+0.159	23	+0.487	23	+0.478	23	+0.450	23	+0.348	24	—0.297	21.5	+0.070	22.8	0.0087
	32	none	23	+0.168	23	+0.502	23	+0.490	23	+0.469	23	+0.384	23.2	—0.336	22	+0.082	22.9	0.0041
10:1	4	40	23	+0.103	23	+0.060	23	+0.060	23	+0.058	23	+0.315	22	+0.040	..	.....	22.8	0.0345
	8	80	23	+0.127	23	+0.074	23	+0.069	23	+0.066	23	+0.333	22.6	+0.027	..	.....	22.5	0.0182
	16	160	23	+0.130	23	+0.095	23	+0.089	23	+0.088	23	+0.327	20	—0.379	23	—0.581	22.8	0.0096
	32	320	23	+0.149	23	+0.139	23	+0.161	23	+0.163	23	+0.333	22.8	—0.419	..	.....	22.2	0.0049
5:1	4	20	23	+0.067	23.2	+0.020	22.9	+0.015	23	+0.012	23	+0.231	25	—0.034	22	—0.078	22.8	0.0378
	8	40	23	+0.081	23	+0.025	23	+0.018	22.9	+0.018	23	+0.233	25	—0.012	..	.....	23.8	0.0211
	16	80	23	+0.103	23	+0.039	23	+0.030	22.8	+0.032	22.7	+0.243	24.8	—0.193	..	.....	22.5	0.0106
	32	160	23	+0.122	23	+0.061	22.8	+0.062	23	+0.062	22.9	+0.232	24	—0.432	..	.....	22.8	0.0053
2.5:1	4	10	23	+0.045	23	—0.026	23	—0.030	23	—0.032	23	+0.228	25	—0.052	25	—0.580	22.9	0.0466
	8	20	23	+0.052	23	—0.020	23	—0.024	23	—0.028	23	+0.227	22	—0.144	22	—0.432	22.6	0.0242
	16	40	22.5	+0.067	23	—0.009	23	—0.012	23	—0.013	23	+0.251	23	—0.147	23	—0.775	23.8	0.0129
	32	80	23	+0.085	23	+0.010	23	+0.006	23	+0.005	23	+0.251	23	—0.437	23	—0.772	23.1	0.0066
1:1	4	4	23	—0.008	23	—0.092	23	—0.097	23	—0.099	23	+0.228	23	—0.197	23	—0.847	22.6	0.0695
	8	8	23	+0.005	23	—0.078	23	—0.082	23	—0.084	23	+0.231	23.4	—0.205	23	—0.823	22.6	0.0364
	16	16	23	+0.023	23	—0.063	23	—0.067	23	—0.071	23	+0.230	23	—0.207	23	—0.829	22.5	0.0193
	32	32	23	+0.039	23	—0.046	23	—0.050	23	—0.052	23	+0.230	22	—0.366	22	—0.768	23.2	0.0100
1:2	4	2	23	—0.063	23	—0.148	23	—0.161	22.8	—0.162	22.8	+0.177	22	†—0.300	22	†—0.908	22.5	†0.0702
	8	4	23	—0.044	22.8	—0.128	23	—0.135	23	—0.139	22.5	+0.183	22.5	‡—0.765	22.4	‡—0.874	22.6	‡0.0442
	16	8	23	—0.024	23.2	—0.106	23	—0.113	22.8	—0.117	22.8	+0.195	21	—0.766	21	—0.840	22.8	0.0272
	32	16	23	—0.004	23	—0.079	22.8	—0.093	23.2	—0.095	22.8	+0.212	21	—0.806	21	—0.848	22.6	0.0142

* N/10 $KAg(CN)_2$ † N/6 $KAg(CN)_2$ N/3 KCN ‡ N/10 $KAg(CN)_2$ N/5 KCN

TABLE II.

Single potentials in double cyanide solutions containing free cyanide and potassium chloride or hydroxide. Temperature 23° C. unless otherwise stated.

RATIO	DILUTION				ELECTRODE POTENTIALS									Specific Conductivity	
	Potassium Silver Cyanide	Free Potassium	Potassium Chloride	Potassium Hydroxide	Mercury Volts	Silver Volts	Copper Volts	Brass Volts	Iron Volts	Zinc Temp.	Zinc Volts	Amalgamated Zinc Temp.	Amalgamated Zinc Volts	Temp.	Mhos
5:1:5	4	20	4	*	+0.089	+0.023	+0.016	+0.015	+0.145	23.2	—0.400	22.2	—0.448	22.2	.0742
	8	40	8	*	+0.091	+0.025	+0.024	+0.024	+0.145	22	—0.482	22	—0.694	22	.0396
	16	80	16	*	+0.099	+0.042	+0.037	+0.037	+0.172	22	—0.494	22	—0.678	22	.0203
	32	160	32	*	+0.120	+0.066	+0.062	+0.062	+0.175	18	—0.500	18	—0.598	18	.00975
1:1:1	4	4	4	*	—0.008	—0.090	—0.097	—0.097	+0.073	20.2	—0.319	20.2	—0.893	20.2	.1015
	8	8	8	*	+0.007	—0.076	—0.080	—0.080	+0.081	21	—0.438	21	—0.802	22.7	.0534
	16	16	16	*	+0.023	—0.060	—0.066	—0.070	+0.161	21	—0.458	21	—0.770	22.8	.0278
	32	32	32	*	+0.037	—0.041	—0.049	—0.049	+0.184	21.2	—0.758	21.2	—0.766	21.8	.0139
5:1:5	4	20	*	4	+0.088	+0.029	+0.022	+0.020	+0.122	21.6	—0.268	21.6	—0.398	22.8	.0667
	8	40	*	8	+0.090	+0.025	+0.025	+0.023	+0.174	22.1	—0.238	22.1	—0.338	22	.0337
	16	80	*	16	+0.106	+0.041	+0.041	+0.038	+0.188	..	.....	..	.....	22	.0171
	32	160	*	32	+0.119	+0.069	+0.069	+0.070	+0.195	..	.....	..	.....	22	.0088
1:1:1	4	4	*	4	—0.017	—0.084	—0.091	—0.093	+0.072	..	.....	..	.....	22.6	.0997
	8	8	*	8	+0.016	—0.067	—0.076	—0.082	+0.087	..	.....	..	.....	23.1	.0481
	16	16	*	16	+0.038	—0.051	—0.063	—0.070	+0.108	..	.....	..	.....	22.9	.0277
	32	32	*	32	+0.040	—0.040	—0.051	—0.061	+0.133	..	.....	..	.....	22.7	.0137

* None.

and the more dilute solutions tested in order to determine the effect of dilution. Cyanide baths are worked at varying concentrations, according to the literature, but it is believed that the range covered by these measurements—from N/4 to N/32 in the double cyanide, that is, from a 5 to 0.625 percent solution of this salt, or from 3.6 to 0.45 oz. metallic silver per gallon (39 to 4 g. per liter)—represents ordinary practice.[12]

Tables I and II contain the figures obtained. Under "Dilution" the numbers represent the volume (in liters) containing one gram molecule of the salt. For conversion to the English system the numbers under this head give the number of gallons containing respectively 14.43 oz. (av.) metallic silver, 8.7 oz. pure potassium cyanide (free), 9.96 oz. potassium chloride or 7.49 oz. potassium hydroxide.

It will be noted in Table I that the pure double salt was first used, and then solutions containing it and various proportions of excess cyanide. In a given series the ratio of the double salt to excess cyanide was kept constant, and is shown in the column "Ratio." The amounts of excess cyanide used were varied from none to twice the amount required to dissolve the silver cyanide present, and should practically cover the commonly used proportions when the bath is made from silver cyanide and potassium cyanide. If the bath is made, as frequently recommended, by dissolving silver chloride in an excess of potassium cyanide, there will always be present in the solution an amount of chloride equivalent to the silver present, assuming that the bath is kept at a constant strength by the use of proper anodes and no more salts added. This condition has been studied and the results are given in the first four series in Table II, where it will be noted that the chloride and silver are always present in equivalent proportions and the excess cyanide is varied from five to fifty percent of the total cyanide required to dissolve the silver chloride, or from ten to one hundred percent of the cyanide required to dissolve an amount of silver cyanide equivalent to the silver chloride used. Similarly, the last two series of Table II show the results when KOH is present, as it would be if silver oxide were used instead of silver cyanide for making up the bath, as often recommended. As before, the hydroxide and silver are in equiva-

[12] Hogaboom, Trans. Am. Electrochem Soc., 23, 288 (1913).

lent proportions, but the variation of proportion of cyanide is only from ten to fifty percent of the amount required to dissolve the silver oxide.

The silver electrode used was a piece of platinum foil, fused into a glass tube, and plated on all exposed surfaces with a heavy coat of silver from a pure double cyanide bath, using a platinum anode. Copper, iron and zinc were commercially pure materials. The brass was in the form of a piece of wire cemented into the end of a glass tube and had the following composition:

Pb	0.5	percent.
Cu	65.5	"
Zn	33.5	"

It is hoped that the influence of other salts in the bath may be studied later in this laboratory, but lack of time prevented any more being included in this paper.

FIG. 1.

Effect of Free Cyanide on the Potential of Silver.

Table III gives differences in potential between silver and other electrodes in solutions of potassium silver cyanide with varying quantities of free potassium cyanide. A negative sign indicates that the electrode is more negative than silver; a positive sign, the opposite. Dilution in liters per gram-molecule.

TABLE III.

Dilution		Electrode Potentials			
Potassium Silver Cyanide	Free Potassium Cyanide	Mercury	Copper	Brass	Iron
2	....	—0.229	—0.003	—0.008	—0.051
4	....	—0.271	—0.006	—0.015	—0.071
10	....	—0.303	—0.009	—0.013	—0.090
16	....	—0.328	—0.011	—0.037	—0.139
32	....	—0.334	—0.012	—0.033	—0.118
4	40	+0.043	±0.000	—0.002	+0.255
8	80	+0.053	—0.005	—0.008	+0.259
16	160	+0.035	—0.006	—0.007	+0.232
32	320	+0.010	+0.022	+0.024	+0.194
4	20	+0.047	—0.005	—0.008	+0.211
8	40	+0.057	—0.007	—0.007	+0.208
16	80	+0.064	—0.009	—0.007	+0.204
32	160	+0.061	+0.001	+0.001	+0.171
4	10	+0.071	—0.004	—0.006	+0.254
8	20	+0.072	—0.004	—0.008	+0.247
16	40	+0.076	—0.003	—0.004	+0.260
32	80	+0.075	—0.004	—0.005	+0.241
4	4	+0.084	—0.005	—0.007	+0.320
8	8	+0.083	—0.004	—0.006	+0.309
16	16	+0.086	—0.004	—0.008	+0.293
32	32	+0.085	—0.004	—0.006	+0.276
4	2	+0.083	—0.013	—0.014	+0.325
8	4	+0.084	—0.007	—0.011	+0.311
16	8	+0.082	—0.007	—0.011	+0.301
32	16	+0.075	—0.014	—0.016	+0.291

Table IV on the next page shows differences in potential between silver and other metals in solutions of silver potassium chloride, with varying proportions of free cyanide, potassium chloride and potassium hydroxide. A negative sign indicates that the metal is more negative than silver; positive, the opposite. Dilution in liters per gram-molecule.

TABLE IV.

Dilution				Electrode Potentials			
Potassium Silver Cyanide	Free Potassium Cyanide	Potassium Chloride	Potassium Hydroxide	Mercury	Copper	Brass	Iron
4	20	4	*	+0.066	—0.007	—0.008	+0.122
8	40	8	*	+0.066	—0.001	—0.001	+0.120
16	80	16	*	+0.057	—0.005	—0.005	+0.130
32	160	32	*	+0.054	—0.004	—0.004	+0.109
4	4	4	*	+0.082	—0.007	—0.007	+0.162
8	8	8	*	+0.083	—0.004	—0.004	+0.157
16	16	16	*	+0.083	—0.006	—0.010	+0.221
32	32	32	*	+0.078	—0.008	—0.008	+0.225
4	20	*	4	+0.059	—0.007	—0.009	+0.093
8	40	*	8	+0.065	±0.000	—0.002	+0.149
16	80	*	16	+0.065	±0.000	—0.003	+0.147
32	160	*	32	+0.050	±0.000	+0.001	+0.126
4	4	*	4	+0.067	—0.007	—0.009	+0.156
8	8	*	8	+0.083	—0.009	—0.015	+0.154
16	16	*	16	+0.089	—0.012	—0.019	+0.159
32	32	*	32	+0.080	—0.011	—0.021	+0.173

*None

The curves in Figs. 1-7 show graphically the results of the work. Fig. 1 shows the effect of the free cyanide on the single potential of silver in solutions of silver potassium cyanide. It is evident that the addition of only ten percent of free cyanide to a pure solution of the double salt increases to a very marked degree the tendency of the silver to dissolve in the solution, as shown by the fact that the silver becomes over 0.3 volt more negative. The difference is evidently due to a decided impoverishment of the solution in silver ions. This is easily determined by calculating the silver ion concentration at 23° for the solutions by means of the well-known formula:

$$E = 0.0587 \log \frac{1}{c}$$

where E represents the electromotive force existing between a silver electrode in a solution normal in silver ions and a silver electrode in the given solution. From the calculations of Abegg,

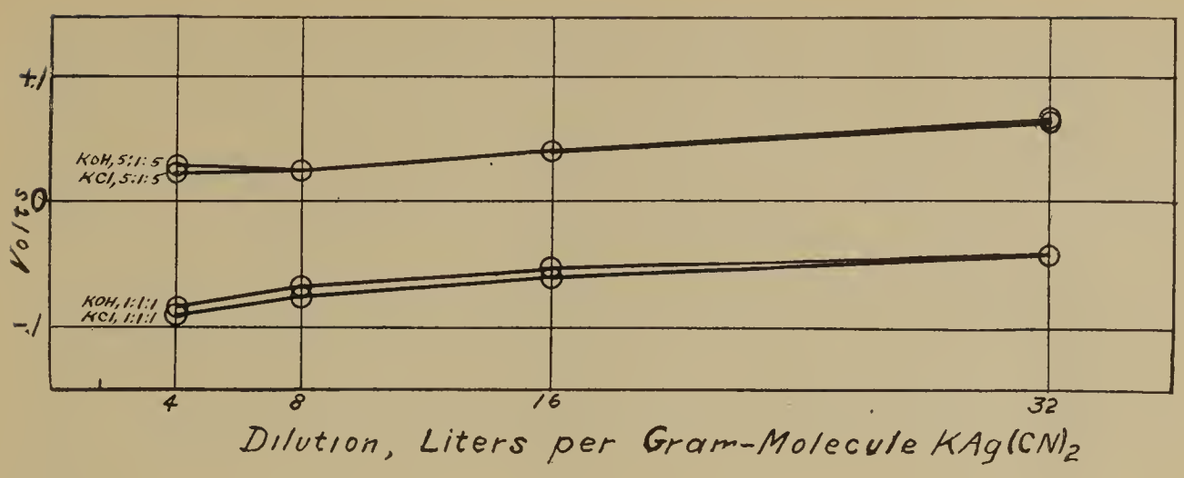

FIG. 2.
Effect of Potassium Chloride and Hydroxide on the Potential of Silver.

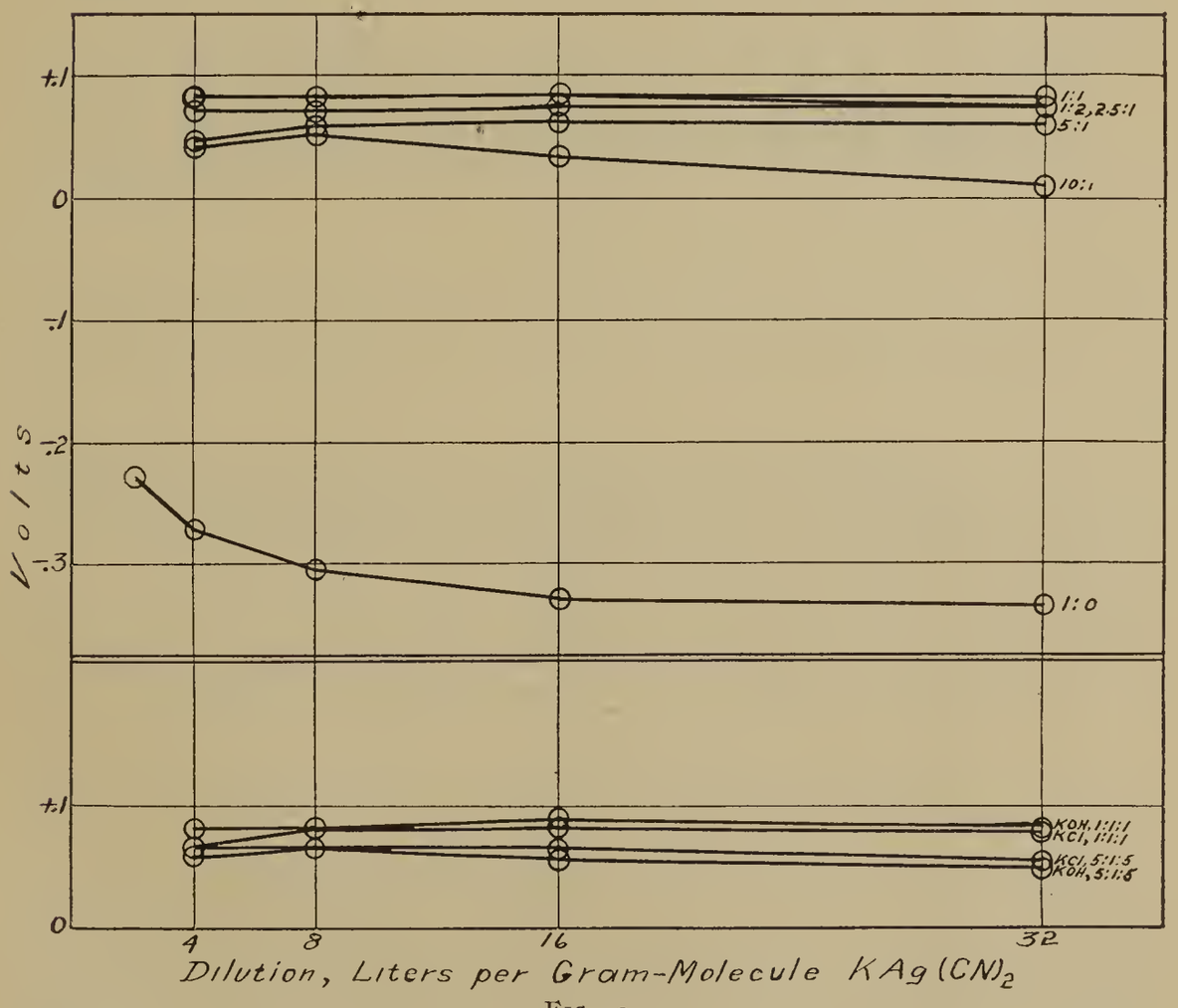

FIG. 3.
Effect of Free Cyanide (Upper Set of Curves), or Free Cyanide Plus Either Chloride or Hydroxide (Lower Set), on the Potential of Mercury Against Silver.

Auerbach and Luther,[13] a silver electrode in a solution normal in respect to the silver ion has a potential, referred to the calomel electrode, of + 1.08 volts. Assuming this value and calcu-

[13] Abhandlungen d. deutschen Bunsen Ges., No. 5, 196.

lating the silver ion concentration from the measurements we have made, we find that in the N/4 solution of silver potassium cyanide it is 7.9×10^{-12}, while the solution containing the same proportion of this double salt, but in addition N/40 free potassium cyanide, has a silver-ion concentration of only 4.27×10^{-18}, or only a little over one two-millionth as much.

Calculation of the silver-ion concentrations for the various solutions reveals another very peculiar fact. In all the solutions the silver-ion concentration actually increases on dilution. This

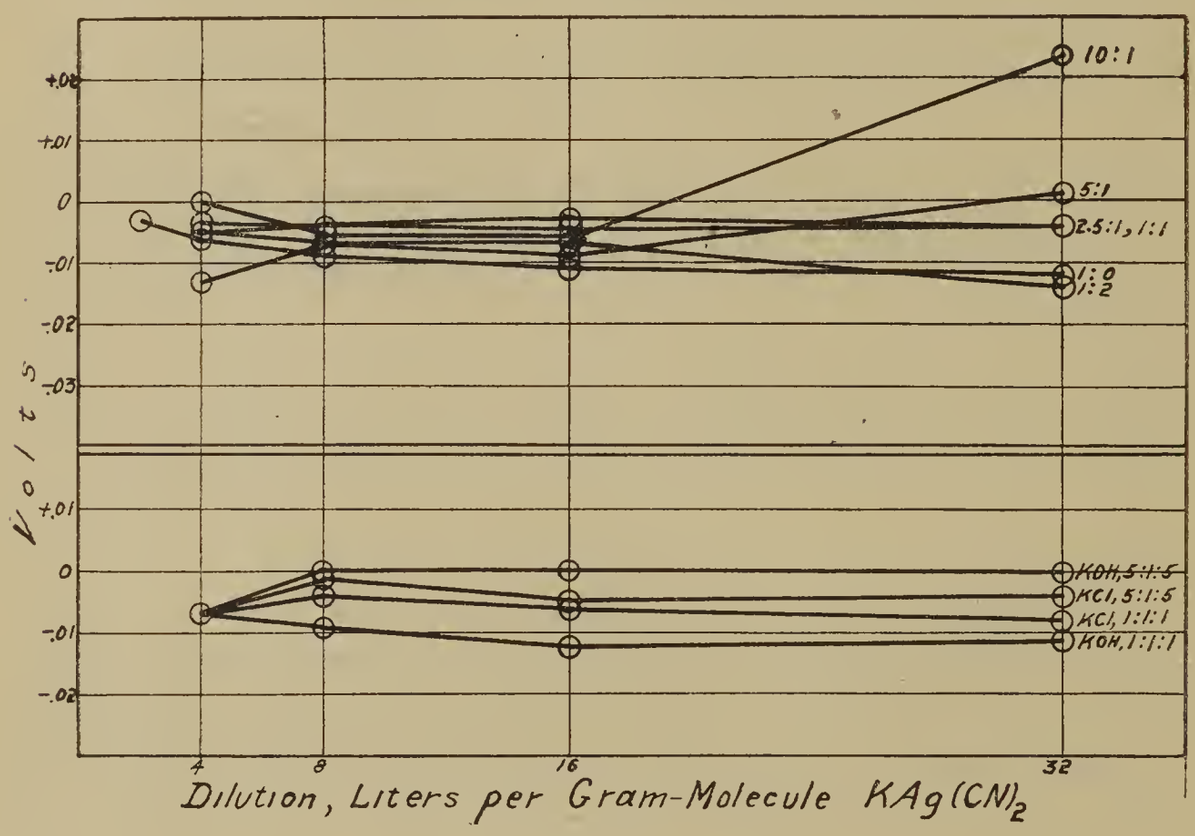

FIG. 4.

Effect of Free Cyanide (Upper Set of curves), or Free Cyanide Plus Either Chloride or Hydroxide (Lower Set), on the Potential of Copper Against Silver.

increase is most marked in the solutions containing no free cyanide, and becomes less marked as the proportion of cyanide increases. In the solution containing no free cyanide, for instance, the silver-ion concentration increases from 2.3×10^{-12} at N/4 to 135×10^{-12} in the N/32 solution. This is undoubtedly due in part to the effect of the dilution on the hydrolysis of potassium cyanide.

In Fig. 2 the silver potentials are plotted as obtained in the presence of potassium chloride and hydroxide. It will be noticed

that there is very little difference between the curves here and those in Fig. 1 for the same ratios of free cyanide to double salt, and we can logically conclude that the presence of hydroxide or chloride in the solution does not appreciably affect the solution tension of the silver.

In Figs. 3, 4, 5, and 6 we have plotted the potentials of mercury, copper, brass and iron against silver in these solutions. In

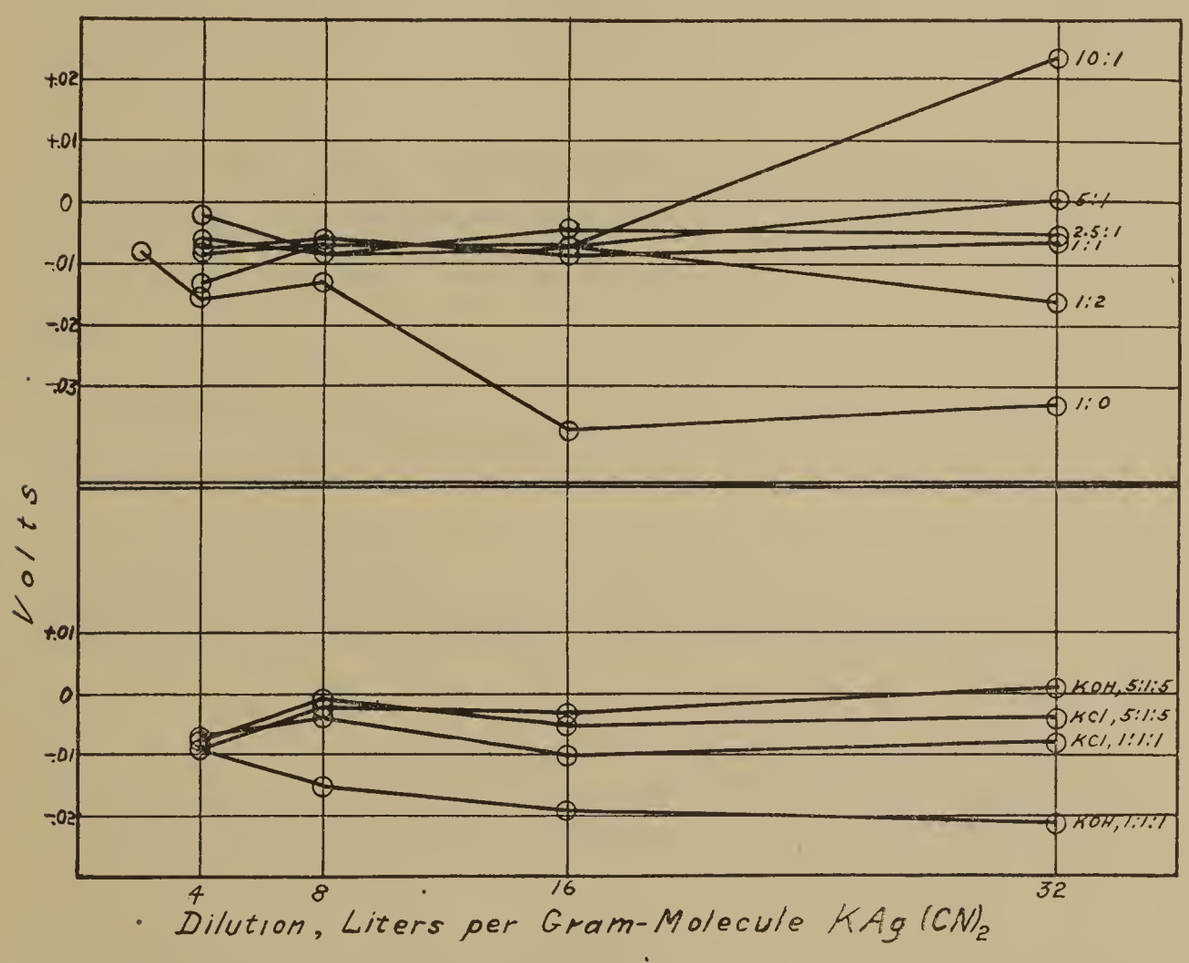

FIG. 5.

Effect of Free Cyanide (Upper Set of curves), or Free Cyanide Plus Either Chloride or Hydroxide (Lower Set), on the Potential of Brass Against Silver.

each figure the upper set of curves shows the relationship when only the pure double salt and potassium cyanide are present, while the lower set shows the effect of potassium chloride and hydroxide, present in the same molecular concentration as the double salt. This corresponds to a bath made by dissolving silver chloride or oxide in an excess of potassium cyanide.

In Fig. 3 it will be noticed that the presence of free cyanide seems to make a great difference in the potential of the mer-

cury, changing it from about — 0.3 volt to a positive value, which increases slightly with increase of free cyanide. The values obtained in the presence of chloride and hydroxide do not differ appreciably from those obtained without them.

Fig. 4 shows that the copper potential is not affected by the presence of the chloride or hydroxide, and Fig. 5 shows that the same statement is nearly true of brass, although the curve for the 1 : 1 : 1 mixture containing the hydroxide may indicate an effect of this substance in the presence of a large quantity of

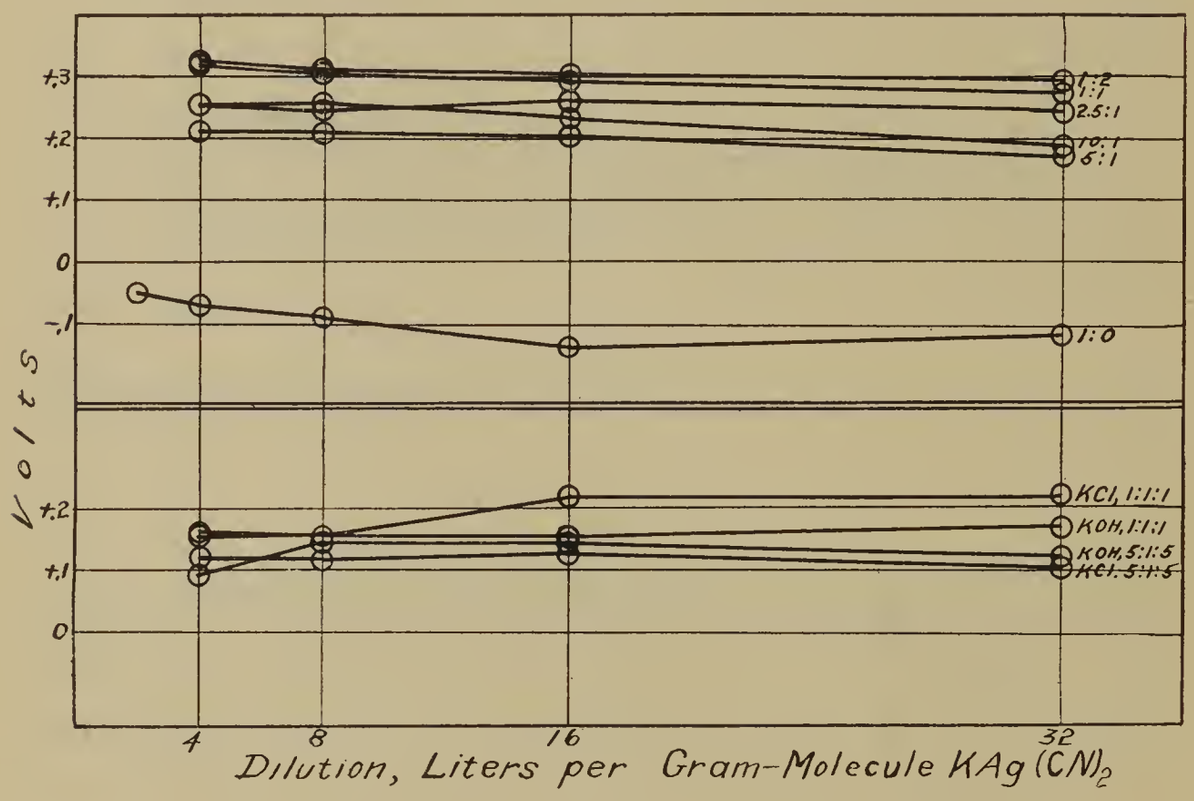

FIG. 6.

Effect of Free Cyanide (Upper Set of Curves), or Free Cyanide Plus Either Chloride or Hydroxide (Lower Set), on the Potential of Iron Against Silver.

cyanide. In this figure, also, the effect of the free cyanide is noticeable and in the same direction as in the case of the mercury, as will be seen from the position of the line for the 1 : 0 (pure double salt) mixture.

Fig. 6 shows the relations for iron. Here again the pure double salt gives values which make the metal negative to silver, while the addition of free cyanide reverses the polarity. Here the chloride and hydroxide seem also to have a definite effect, making the iron about 0.1 volt less positive to the silver than it was when these salts were not present.

In Fig. 7 the specific conductivity has been plotted, and it will be seen that the chloride and hydroxide have a very decided effect in increasing the conductivity, as was to be expected. In general, the chloride has a slightly greater effect in this direction than the hydroxide. Excess of free cyanide increases the conductivity to approximately the same extent as the chloride or hydroxide; since all of these have a similar effect on the specific gravity of the solution, it appears to be approximately correct to regard the gravity as a rough measure of the conductivity of the bath.

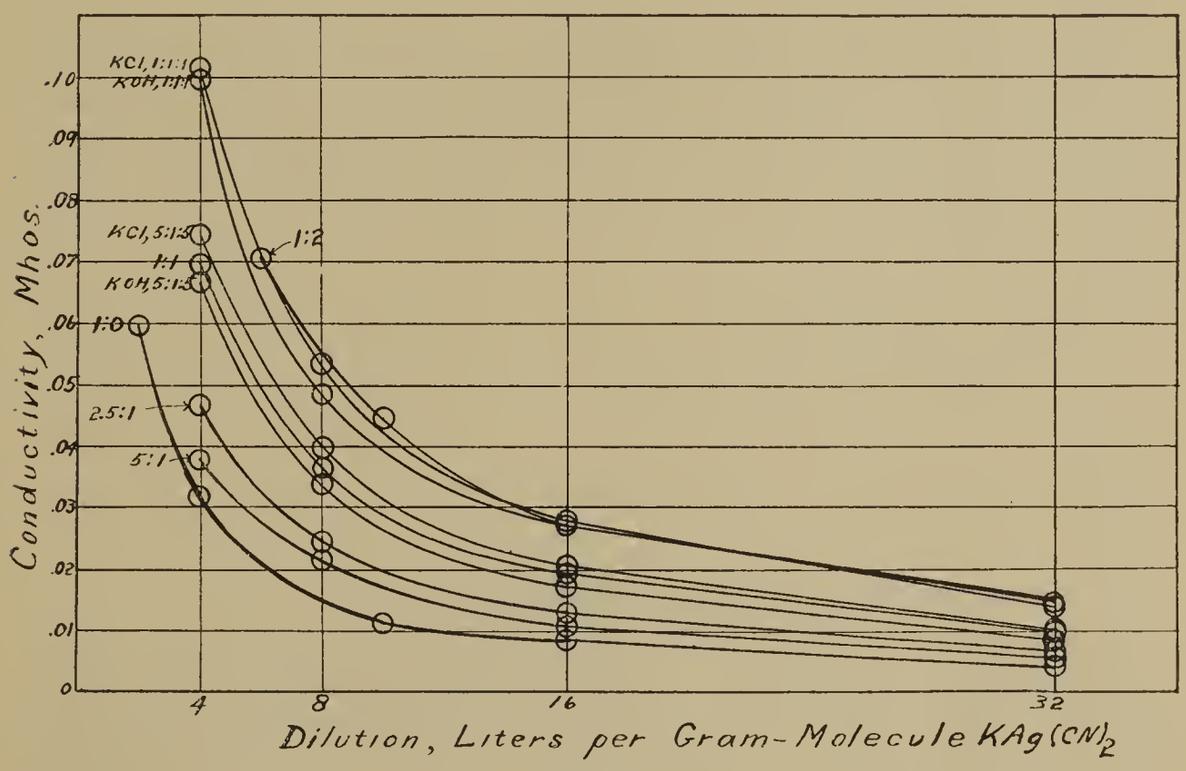

FIG. 7.

Conductivity of Solutions Containing Potassium Silver Cyanide, Free Cyanide, etc.

SUMMARY AND CONCLUSIONS.

The single potentials of mercury, silver, copper, brass, and iron in solutions of potassium silver cyanide with various proportions of excess cyanide, with and without chloride and hydroxide equivalent to the silver, have been determined and compared, and the conductivities of the solutions determined. The values for iron and brass are a little uncertain; the former on account of delay in attaining equilibrium and probably also on account of the difficulty of obtaining a reproducible electrode, and the latter because the effect of the free zinc in the alloy

could not be determined. Some determinations made on zinc electrodes show that this metal is decidedly negative in respect to silver, as was to be expected.

Copper and brass are evidently only slightly negative to silver in these solutions, and their relation is not affected by the presence of chloride or hydroxide in the proportions studied.

Iron and mercury are definitely positive to the silver, whenever at least 10 percent of free cyanide is present, but negative to it in the absence of free cyanide. Mercury is not affected by the presence of chloride or hydroxide, but the iron is made about 0.1 volt less positive.

It appears probable that titration of potassium cyanide with silver nitrate according to Liebig gives results which are low, to the extent of about three percent of the cyanide present. Titration with mercuric chloride gives results which appear more nearly correct.

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DISCUSSION.

President L. Addicks: I think this paper is open to one criticism, and that is that we really have two papers here on practically unrelated subjects. The first is on the question of proper assay method for obtaining cyanide, which has no relation whatever to the other paper. I never look over a paper of this character without realizing how little we know of the early character of electric plating. Only lately we have seen what a great difference the electrolyte makes in the separations that we get. Also, we see statements of the different effects we get from the solutions just made, and then after the solution has been used for several weeks or a month, which is another way of saying that small quantities of impurities make a great difference in the result that we get afterwards at the anodes.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

ELECTROLYTIC ANTIMONY REFINING.

By Anson G. Betts.

It is already known that antimony may be electrolytically deposited in a very satisfactory mechanical condition from the fluoride solution, and that the deposit does not carry down antimony salt with it, as the deposit from the chloride solution is apt to do. I have shown that the fluoride solution, for an easy anode reaction, should not contain sulphates or other oxygen acids, or their equivalents, because the anode reaction tends to the formation primarily of antimony sulphate, for example, which quickly decomposes into an insoluble basic sulphate.* This material insulates the anode surface, and by raising the electromotive force helps the solution of the less-readily attacked constituents of the anode. The fluorine anion is relatively sluggish, and in presence of the more easily transported sulphion, for example, forms at the anode a small proportion only of the directly soluble antimony fluoride. To achieve at once complete solution of the anode as fluoride, it is necessary to exclude all other anions from the solution.

It has not been known how the impurities of the antimony anodes will behave. Lead can be expected to form lead fluoride, which by reason of its insolubility may remain largely in the anode slime. Bismuth also makes an insoluble fluoride in the presence of free hydrofluoric acid, and in the absence of stronger acids, and may be expected to remain in the anode slime, if the solution is rightly proportioned.

Silver stands about 0.6 volt below antimony in the scale of electromotive forces of solution, and could only be expected to remain in the anode residue as metal; gold would, of course, act likewise, and for the same reason.

Copper is readily dissolved as anode in a fluoride solution, and stands so near antimony in the scale that it might seem

* Trans. Am. Elecrochem. Soc., 8, 187 (1905).

unlikely that copper would remain undissolved if there is the usual polarization voltage at the anode surface of 0.1 to 0.2 volt, even with a pure fluoride solution. It will be shown by what follows that generally copper does not dissolve at the anode, and knowing the ready solubility of copper fluoride, we can be quite sure that the copper remains in the slime in the metallic condition.

Arsenic is also very near to antimony in the electrochemical scale, and is thought to have a higher deposition voltage than antimony. One would expect that arsenic would dissolve from the anode, and not depositing so rapidly as the antimony, would accumulate in the solution until by virtue of its increasing concentration it finally deposited in the cathode metal as fast as it dissolved from the anode. This expectation was not realized experimentally.

EXPERIMENTAL.

The first experiment was made in a paraffined wood cell holding about 1500 c.c., fitted with a stirrer which at times stopped working and affected the experiment, but not seriously.

The anode was 1 x 4.25 x 6 inches (2.5 x 10.5 x 15 cm.) and weighed 3655 grams. Analysis showed it to contain:

Silver	0.092	percent
Antimony	74.79	"
Arsenic	11.88	"
Lead	3.98	"
Copper	3.25	"
Iron	0.16	"
Bismuth	2.58	"

The solution was made up to contain in 100 c.c., 10 grams of antimony as trifluoride, besides potassium fluoride and hydrofluoric acid in the proportions given by the formula SbF_3. KF.HF. The mixture crystallized partly, so the solution was not as strong as was intended.

The cathodes were of copper, spaced about one inch (2.5 cm.) from the surfaces of the anode. The current used varied from two to three amperes, and mostly it was very near 2.1 amperes, corresponding to a current density of 6.6 amperes per square foot, or 73 amperes per sq. metre. The electromotive force was near 0.6 volt, but this increased after two or three days, as the slime layer grew thicker. The slime was removed occasionally,

to prevent this undue voltage with the consequent increased solution of impurities from the anode that one would expect. The deposited metal was removed from the cathodes frequently, and the percentage of impurity it contained was determined. No appreciable quantity of impurity was found in any of it, except 0.35 percent Pb, and considerable As. The principal results are shown graphically in Fig. 1. It was noted that the percentage of As in the metal deposited only varied a little, depending on the rate of circulation to a slight extent, but more on the current density and on the amount of slime on the anode.

The amount of arsenic in the solution at all times was small,

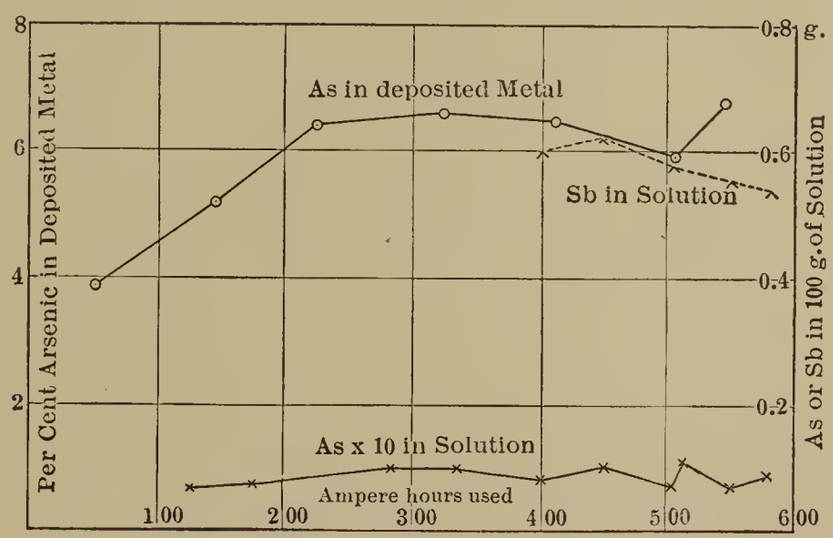

FIG. 1.

the amount being plotted in Fig. 1. Comparatively, the As is far more concentrated in the cathode metal than in the solution, which shows it to be more readily precipitated than antimony. As/Sb in cathode metal approximated to 0.065, while As/Sb in solution approached 0.016.

The deposited metal was at all times hard, solid, and non-projecting.

The principal conclusions to be drawn are: (1) there is no difficulty in eliminating lead, bismuth, and copper under these conditions, which are rather severe with so low a proportion of antimony in the anode metal; (2) the solution does not become contaminated with impurities; (3) the physical condition of the deposit is all that could be desired; (4) the required current density is less than is desired and generally used for other metals,

and the voltage is a good deal higher; (5) only about half the arsenic could be kept in the anode slime.

The additional analyses which were made in connection with the experiment are:

SLIME.

	1 Percent	2 Percent	3 Percent	4 Percent	5 Percent
Arsenic	19.6	....	18.06	17.46	....
Antimony	28.1	....	21.17	24.57	....
Lead	15.4	....	14.3	14.2	....
Copper	10.6	....	16.3	16.0	....
Bismuth	9.85	13.5	13.1	11.7	....
Iron	Trace	....	....	....	....
Silver	....	....	....	....	....
Amount	48 gr.	30 gr.	39 gr.	46 gr.	36 gr.

DEPOSITED METAL.

	1 Percent	2 Percent	3 Percent	4 Percent	5 Percent	6 Percent	7 Percent
Arsenic	3.89	5.18	6.36	6.59	6.45	5.92	6.81
Antimony	94.73	93.32	91.97	91.33	91.88	....	....
Lead	....	....	....	....	0.35	....	....
Copper	....	....	....	....	None	....	....
Bismuth	....	....	....	....	None	....	....

Samples of the cathode metal for analysis were fused under KCN, before the analyses. The weight of anode decomposed was 853 grams, and of metal deposited, about 675 grams. There was 199 grams of slime produced. Some metal was found in the bottom of the cell.

In the preceding experiment the anode contained a larger percentage of impurity than is usual in electrolytic refining of metals. As it was impossible to conclude that with an anode containing less impurity arsenic would remain entirely, or in larger proportion, in the anode residue, another experiment was necessary.

Part of the old anode was melted with an equal quantity of fresh antimony, and was cast into a new anode, which should have had about the following composition. (It was not analyzed).

Antimony	87.5	percent
Arsenic	5.95	"
Lead	2.0	"
Copper	1.65	"
Bismuth	1.3	"
Iron	0.16	"

The solution and cathodes were the same as were used in the former experiment. The current density was about 6 amperes per square foot, and electromotive force 0.6 to 0.65 volt. The electrolysis was continued for about 36 hours, and 250 grams of the anode was decomposed, while 221 grams was deposited on the cathodes. The anode slime was very soft and readily removed, and did not interfere with the solution of the metal underneath, as was the case in the first experiment.

The electrolyte was analyzed at intervals for As, which was found to amount to 0.06 gram As per 100 c.c. during the entire experiment. The first 143 grams deposited contained As, 4.23 percent; Cu, Pb, Bi, none, and the 78 grams following contained 3.93 As, with no Cu, Pb or Bi. The 25 grams of slime contained 13.9 percent As and 25.3 percent Sb.

The conclusions are these: (1) with an anode of this composition the electrolysis goes smoothly, and there is no need of scraping the anode slime from the anodes; (2) a larger proportion of the arsenic goes over into the cathodes, viz.: 60 percent as against about 40 percent of the total As in the first experiment. The deposit was physically good, perhaps a little better than before. Cu, Pb and Bi may be thus separated from antimony.

When a solution of arsenious chloride is heated with metallic copper, a black arsenide of copper is precipitated on the copper. To learn whether the presence of copper would tend to retain arsenic in the anode slime as an arsenide of copper, thus yielding a purer antimony deposit at the cathode, an anode was made containing about

Antimony	84.8	percent
Arsenic	5.4	"
Lead	1.8	"
Copper	6.65	"
Bismuth	1.2	"

In refining this anode, the solution and conditions were the same as in the preceding experiment, except that the stirring was even more vigorous this time. At the end of 31 hours, the solution contained 0.045 percent As and the deposited metal 3.15 percent As, with only a trace of copper.

The result shows the effect of copper in holding back arsenic in the slime to be certainly small, if there is any such effect at all.

Following up the discovery that arsenic tends to deposit from the fluoride solution more rapidly than antimony, in proportion to the quantities present, it becomes important to know if in depositing antimony from the fluoride solution containing sulphuric acid, with an insoluble lead anode, as is sometime done in treating lead-refinery anode slime, the arsenic present in solution could not be collected with the first part of the antimony, thus producing the latter, and perhaps, greater part of the antimony in pure form.

1400 c.c. of solution was used containing about 124 grams of antimony and 5.3 grams of As as trifluorides, one or two grams HF, and 65 grams H_2SO_4; or per 100 c.c. Sb 8.85 grams, As 0.38 grams, HF about 0.1 gram, H_2SO_4 4 grams. The solution was electrolyzed at the ordinary temperature with two copper cathodes, having an active area of 24 square inches (150 sq. cm.), and with a lead anode, cotton-covered, having an active area of about 2.5 square inches (15.6 sq. cm.). The current was 1.2 amperes, or a cathode current density of 7.2 amperes per square foot (80 per sq. m.).

Analysis of the solution was made at intervals for antimony and arsenic, the difference between two consecutive analytical results showing the quantities deposited. The results are plotted as Fig. 2, in which the curves show grams of antimony, and twenty times the grams of arsenic, each per 100 c.c.

Only one analysis of deposited metal was made, that of the first 9 grams deposited, which contained 5.0 percent As. The proportion of As to Sb at the start was 4.3 percent.

Referring to the figure, the Sb and As curves, up to 34 ampere hours, show that the Sb and As are depositing out in very nearly the same proportion as they exist in the solution. If any separation of the two were practicable in this way, the favorable conditions of this experiment, low current density, and very good circulation, should show it. During the experiment the rate of circulation was changed to see if it made any difference, but none was detected.

After about 34 ampere hours of current passed, and it was seen that no practicable separation of As and Sb was indicated

with this solution, copper sulphate was added to the solution, to see if copper in depositing would have any tendency to carry As out with it.

The conclusion of the experiment showed that copper has a tendency to do this, but the effect is too small to be of any use.

The continuation of the Sb curve in a dotted line is derived by subtracting from the antimony found by analysis, the antimony equivalent of the copper added.

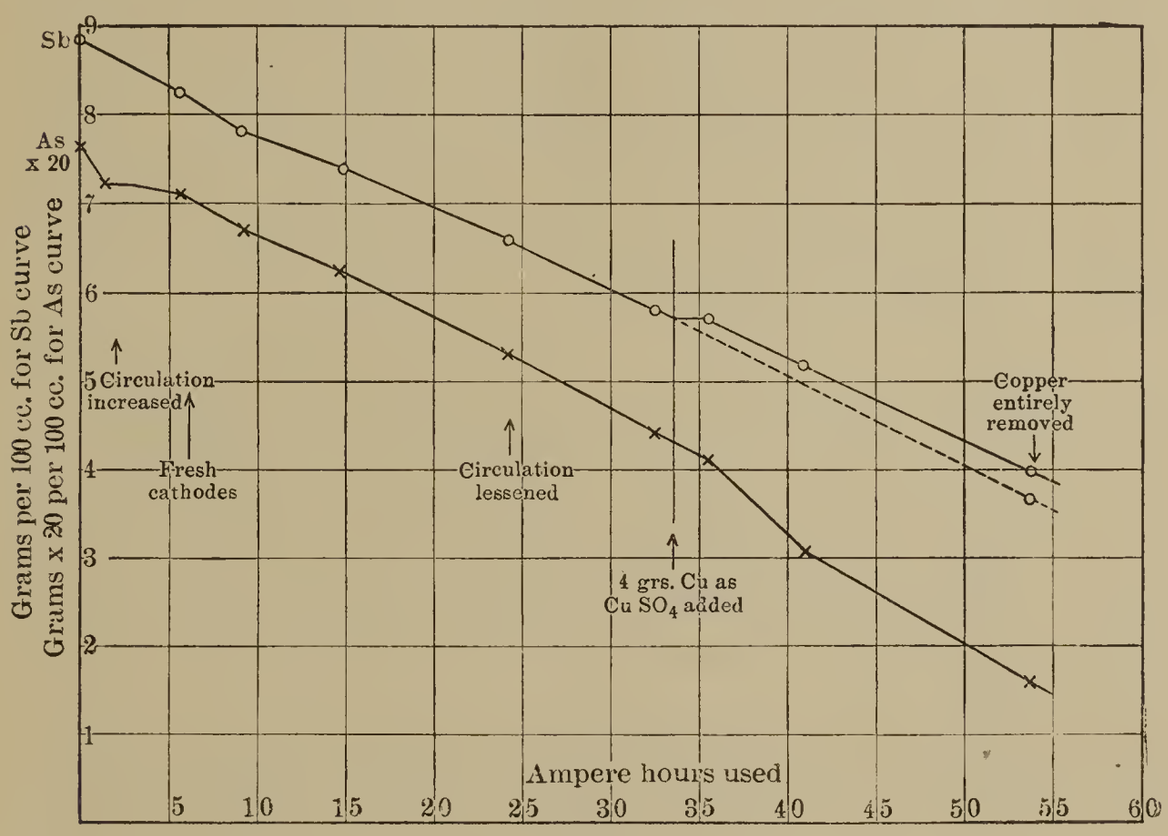

FIG. 2.

Calculating the ratios of antimony and arsenic in the deposited metals and in the solution, in the beginning of this experiment they are respectively about 19.1 and 23.1, so that the relative speed of deposition of antimony and arsenic in proportion to the amounts present, is about 1 : 1.2.

With the solution used in the antimony refining experiments, the principal difference being that the refining solution contained no sulphuric acid, the corresponding ratio is about 1 : 4.2. The presence of sulphuric acid interferes to a large extent with the tendency toward separation of the two elements.

With such a refining solution as that used in the first experiment described, there is sufficient difference in the behavior of arsenic and antimony to make possible a differentiation of the deposited metal into two parts, one a good deal lower in arsenic and the other higher, by alternately causing the refining solution to circulate rapidly and remain at rest. If the solution were electrolyzed quietly, keeping the anode away from the cathode, and removing a large proportion of the metal from the solution in contact with the cathodes, the deposited metal should contain only about 1 percent of As instead of 6 percent, as the total quantity of As present in the solution is so small. If the solution is then rapidly circulated so that the As brought into solution from the anode could be quickly brought to the cathodes, the proportion of As deposited should be much greater than 6 percent, perhaps as high as 25 percent.

The simplest way in which to carry out this idea of producing two quantities of antimony, one very high and one very low in arsenic, is to cause the solution to pass in turn through a refining cell with strong agitation, and another refining cell with as little agitation as possible, preferably arranged so that the heavy solution running down the anode surface could be collected in the bottom of the quiet cell, and siphoned out into the agitated cell.

The apparatus used consisted of one main wooden cell 38 cm. deep by 12.75 cm. by 20.3 cm., with a capacity of about 10 liters, and a series of four auxiliary cells 12.9 cm. deep by 7.75 cm. by 7.75 cm., with a total capacity of about 3 liters.

The main anode, about 1.8 cm. thick by 15 cm. by 30 cm. was suspended in the middle of the main tank, between two copper cathodes.

The first of the small cells, through which the solution from the main tank passed, contained one anode of the same composition as the main anode, and a copper cathode, the active anode or cathode area being about 6.8 cm. by 10 cm.

In the other three tanks anodes of pure Sb, and Cu cathodes were used, of the same size as those in the first of the small tanks. The alloy to be refined contained:

Antimony	84.0	percent
Arsenic	5.4	"
Copper	3.6	"
Lead	3.7	"
Bismuth	1.1	"

The solution was made to conform to the formula $SbF_3.NaF.KF.HF$, and should have contained 4.4 grams Sb, 1 gram Na, 1.4 grams K, and 0.8 gram HF per 100 c.c. A small quantity of salts crystallized out and a very little solution was spilled, so the solution was undoubtedly somewhat weaker and contained at the end of the experiments only 1.8 percent Sb. This lowering had, of course, resulted from the conversion of the lead in the anode to lead fluoride with the reduction of the corresponding amount of antimony.

Some difficulty was experienced in regulating the flow of solution through the tanks, and the stirrers sometimes stopped during the night.

With an electromotive force of 1.35 volts the large tank used (at about 17° C.) 8.5 amperes, and the four small tanks in multiple about 15 amperes, or current densities of respectively 1.2 and 0.4 amperes per square decimeter (12 and 4 per sq. ft.).

The large tank was fitted with a distributor, so that the heavy solution flowing in from the four small purifying tanks should mix with the light solution at the top of the large refining cell.

The heavy solution running down the anode collected in the bottom of the tank and was continuously removed to the purifying tanks through a rubber tube.

During the first experiment the heavy solution at the bottom of the refining cell and in the purifying cells contained about 6.2 percent Sb, and the solution at the top of the refining cell 3.3 percent Sb.

The character of the deposit in the four purifying cells was different, that in the first cell especially being darker, duller and less crystalline, and containing more As, as was expected.

After three days the solution in the first three of the purifying cells contained:

No. 1	0.148	percent	Arsenic
No. 2	0.133	"	"
No. 3	0.122	"	"

The purification was evidently less complete than could be inferred from the fact that the solution in the first refining experiment contained only about 0.05 percent As.

After five days the upper three-quarters of the main cathode was collected and melted separately from the bottom quarter. The upper 660 grams contained 3.0 percent As and the lower 210 grams contained 3.4 percent As. To the solution was then added enough NaF to correspond to the formula $SbF_3.2NaF.KH.HF$. The solution crystallized a little, so it was taken out, filtered, mixed and analyzed, showing it to contain 0.07 percent As, and put back.

After five days more 1060 grams of cathode metal was found to contain 3.18 percent As.

The following analyses are of the slime produced in the first five days, the second five days, and that taken from the first small cell:

	First Slime	Second Slime	Slime in Small Cell
Arsenic	8.2 percent	8.17 percent	8.5 percent
Antimony	7.16 "	7.94 "	16.7 "
Lead	26.9 "	28.1 "	
Copper	30.1 "	26.2 "	
Bismuth	6.53 "	5.4 "	

Thinking that a diaphragm might keep the impure anode solution in the refining cell away from the cathodes, a muslin diaphragm was used, reaching nearly to the bottom of the cell. The diaphragm was of two or three thicknesses, spaced one-half inch (1.25 cm.) in the clear from the anode surface. The current was reduced to 5.5 amperes for the large cell and 1.5 amperes for the four small cells in multiple. After six days electrolysis the following figures were obtained by analysis of the products:

	Grams	Percent Arsenic
Upper third	240	3.4
Middle third	275	3.3
Lower third	260	3.3
Small tank No. 1	59	4.6
Small tank No. 2	87	3.9
Small tank No. 3	75	3.9
Small tank No. 4	100	3.9

The absence of a diaphragm was evidently not the weak point in the first part of the experiment, as the result was practically the same either way. The percentage of As in the metal deposited in the four small tanks was evidently much less than indicated from the ratio of 1 : 4.2 for As in metal found in the first experiment. The difference must be due to a difference in the temperature, current density, or composition of the solution.

Another run of four days with the addition of four grams HF per liter yielded products analyzing as follows:

	Grams	Percent Arsenic
Main cathode metal	430	3.6
Small tank No. 1	17	6.6
Small tank No. 2	23	6.3
Small tank No. 3	20	6.1
Small tank No. 4	20	5.8
Total of small tanks	80	6.05

The improved, but still unsatisfactory result, is believed to be due to the presence of more HF in the solution.

The solution (now thrown away) contained 1.8 percent Sb and 0.06 percent As giving a ratio calculated as before of 1:2 since

$$\frac{\text{As in solution}}{\text{Sb in solution}} = 0.033 \text{ and } \frac{\text{As in metal}}{\text{Sb in metal}} = 0.066. \quad \text{Ratio is } 1:2$$

It was concluded that a study of the ratio

$$\frac{\text{As in solution}}{\text{Sb in solution}} : \frac{\text{As in metal}}{\text{Sb in metal}}$$

with varying solution composition, temperature, current density, and perhaps other factors is necessary for successful refining by this method.

Experiments were then made to determine the effect of temperature on the amount of As passing over into the cathodes. As there is a counter e.m.f. even with the fluoride solution, sometimes as high as 0.2 volt, it might be possible by raising the temperature to reduce the anode e.m.f. to a point where antimony but not arsenic could be dissolved.

The solution used contained, in 100 c.c., 3 grams NaF, 11 grams SbF_3 and 1 gram HF. Three small rubber jars were arranged as electrolytic cells at temperatures of 30°, 40°, and 50° respectively. The current varied from 1 to 1.4 amperes, correspondingly to a current density per square foot of 14 to 20 amperes, with an e.m.f. per cell of about 0.9 volt. After 43 hours electrolysis the experiment was discontinued with these results:

30° cell short circuited, 35 grams deposited, in smooth condition at the bottom and rough and flaky on top.

40° cell, 54 grams deposited, rather smooth and even throughout.

50° cell, 45 grams deposited, in still smoother condition.

The deposits were melted and analyzed for As, with these results:

Temperature	Arsenic
30°	3.5 percent
40°	3.6 "
50°	3.9 "

I tried the purification of antimony from arsenic by crystallizing the melted metal analogously to the purification of lead and bismuth by crystallization. Numerous experiments with antimony-arsenic alloys containing from 3 to 8 percent of arsenic gave in all cases crystals and liquid portions containing the same percentages of arsenic.

The alkaline sulphide solution of antimony was tried as a refining medium. The solution was made by dissolving 30 grams of SbF_3 in 500 c.c. sodium sulphide solution of specific gravity 1.19. The solution was electrolyzed warm with the same composition of anode as used in the last preceding refining experiments.

After 24 hours' run the cathode deposit averaged 1.0 percent As and after 48 hours 2.1 percent As.

Returning to the original idea of refining in the usual way, with the fluoride solution, some of the refined antimony containing about 3 to 3.5 percent arsenic was cast into an anode, and again refined in the same way. About half of the arsenic remained in the anode slime. By several refinings the arsenic may probably be eliminated.

The most positive reaction noted in these experiments is that due to the composition of the solution. An increase in HF is highly beneficial and the presence of sulphates or sulphuric acid is shown to be objectionable. It is likely that the hydrofluoric acid may have contained traces of sulphuric or fluosilicic acid, and the negative results might have been traced to that cause. The effect of alkaline fluorides and ammonium fluoride should be studied, also.

A successful method of electrolytic refining of antimony should receive technical application, inasmuch as present methods do not save the gold frequently present and are incapable of making a product of a high and uniform grade at all comparable to the copper, lead and silver on the market.

DISCUSSION.

President L. Addicks: I think the title of Mr. Betts' paper is rather a misnomer. In the first place, it is not reasonable refining. The anodes used were so foul that much more than refining is necessary; and in the second place, he did not succeed in the work. The real problem in refining antimony is in getting it away from its neighbor, arsenic, and with the electrolytes used there was no separation at all. This is important only on differences of decomposition voltages to effect separation. He used an electrolyte where arsenic and antimony have practically the same decomposition voltages.

I might say that I was talking recently with Mr. Aldrich, of the Raritan Copper Works. They have done work on this line, and had no success in obtaining such a separation.

A. G. Betts (*Communicated*): I am unable to find in Mr. Addicks' discussion any statements not covered by the paper and cannot see anything wrong with the title, and believe the paper contains information that would be of value to anyone wishing to make further researches in this direction. There is very little

practical or scientific information in the literature relating to the technology of this metal.

In the paper, a new general method for the refining and treatment of alloys has been described, which I have also applied to the refining of nickel-iron alloys, with the result of producing two grades of cathodes, one higher in nickel than the anode, and the other lower. I have also noticed a recent description of the application of this method for treatment of impure copper-refining solutions preparatory to their purification.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

ELECTRODEPOSITION OF NICKEL.

By C. W. Bennett, C. C. Rose and L. G. Tinkler.

In the discussion of the electrodeposition of nickel[1], it was shown that the apparent mysterious results obtained by Calhane and Gammage[2] could be satisfactorily explained on the basis of the electrochemical series. In a solution of nickel ammonium sulphate, there are present hydrogen, nickel, and ammonium ions. Of these the hydrogen ions are liberated most easily. When the electrolysis is started for the deposition of nickel, hydrogen ions, being present, are liberated first, and therefore the efficiency of nickel deposition is low. If the electrolyte and cathode be stationary, there is an impoverishment of hydrogen, with a subsequent deposition of nickel at an efficiency which depends upon the impoverishment of hydrogen or upon the rate of bringing up of hydrogen ions to the cathode. This rate of bringing up hydrogen ions to the cathode may be affected in two ways. First the electrolyte or the cathode may be rapidly moved and therefore diffusion aided. Second, the concentration of hydrogen ions may be increased, therefore the rate of bringing up hydrogen ions increased, because more are present to be brought up.

In previous work on the deposition of nickel the latter condition was studied, the concentration of hydrogen ions were changed by adding ammonium hydroxide to the solution, tending to make it alkaline. Under these conditions it was found that starting with straight nickel ammonium sulphate and measuring the efficiency every fifteen minutes, the efficiency of deposition began at about 87 percent and increased to a fairly definite maximum of about 96 percent. The conditions of such electrolysis were with stationary cathode and stationary electrolyte. When vary-

[1] Jour. Phys. Chem., **18**, 373 (1914).
Trans. Am. Electrochem. Soc., **25**, 335 (1914).
[2] Jour. Am. Chem. Soc., **29**, 1268 (1907).

ing quantities of ammonium hydroxide were added to the solution, the efficiency began higher and reached finally a higher state.

The results obtained by Calhane and Gammage referred to above show that the efficiency of nickel deposition with the rotating cathode was much lower than with a stationary one, and the efficiency decreased as the speed of rotation of the cathode increased.

In previous work it was shown that the surface film at the cathode could be disturbed by stirring the solution as well as by rotating the cathode, and experiments were given showing that

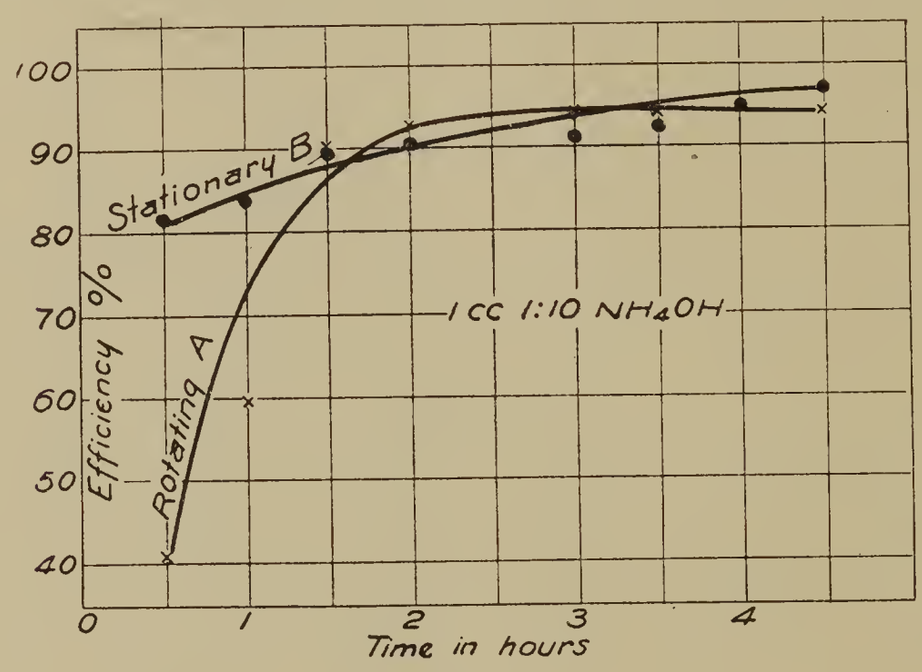

FIG. 1.

the efficiency of deposition is less the more rapidly the solution is agitated.

With reference to the rotating cathode, with which this investigation is concerned, the same methods have been used for changing the concentration of hydrogen ions as were used in the previous work.

If small quantities of ammonium hydroxide be added to the solution with a rotating cathode, the efficiency should be affected in a way analogous to that with a stationary cathode. In other words, it may be expected that the addition of ammonium hydroxide would tend to raise the efficiency of deposition of the rotating cathode as well as of the stationary one, *i. e.*, the efficiency

should start higher and approach the same point or perhaps reach a higher one. Experiments were accordingly made with stationary and rotating cathodes with varying amounts of ammonium hydroxide. 1 c.c., 5 c.c., and 10 c.c. of 1:10 ammonium hydroxide were added to 120 c.c. of the nickel ammonium sulphate solution. This was the same as in the previous work, containing 8 grams of nickel ammonium sulphate with one gram of nickel chloride per 100 c.c. of water. The anodes were all electrolytic nickel, containing 0.14 percent iron.

The current density was approximately 1¼ to 1½ amperes per square decimeter.

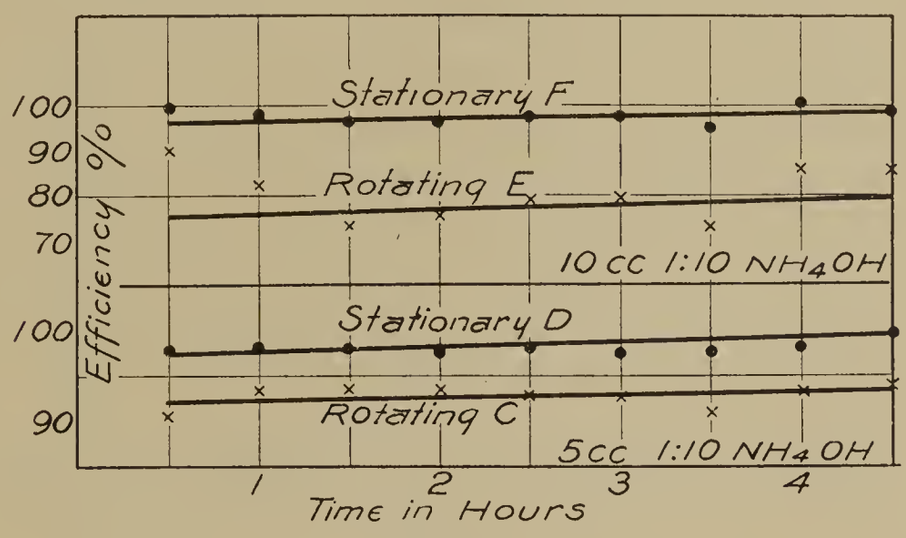

Fig. 2.

The results of one set of experiments are shown in the curves of Figure 1 and Figure 2. Curve A, Figure 1, represents a series of efficiency measurements taken every thirty minutes with a cathode rotating 1,000 revolutions per minute. This cell had 1 c.c. of 1:10 ammonium hydroxide. Curve B shows a cell with a stationary cathode run under the same conditions in series with the first one. Curves C and D, Figure 2, show curves for the rotating and stationary electrodes respectively, with 5 c.c. of 1:10 ammonium hydroxide. Curves E and F show rotating and stationary electrodes respectively with 10 c.c. of 1:10 ammonium hydroxide. From these curves it is evident that if the solution is of the proper alkalinity, the efficiency begins high and is maintained at fairly high value when the cathode is rotated. This is best shown in Curve C.

Having shown that it is possible to increase the efficiency by decreasing the concentration of hydrogen ions, it is only a step theoretically to the extreme condition, where the concentration of hydrogen ions is practically zero. If nickel could be deposited from a strongly alkaline solution or from a solution of nickel in a strong base, the hydrogen ion concentration in this solution would be practically zero. Being practically zero, the agitation of the solution would practically not affect the electrolysis in so far as the hydrogen is concerned. If a solution could be obtained, which has a high concentration of hydrogen ions, agitation of the solution should practically not affect the efficiency. If, on the other hand, the ion concentration is low, agitation of the solution or rotation of the cathode should increase the efficiency over that obtained with a stationary electrode. We are therefore in a position to say that a solution of nickel in a strong base should yield nickel upon electrolysis with the same efficiency or a higher one if the electrode be rotated. In other words, the conditions would be just reversed from those obtained from the nickel ammonium sulphate solution.

A number of solutions were tried before a satisfactory one was obtained. A solution of nickel cyanide was finally used, the solution containing approximately 5 percent nickel cyanide and 7 percent potassium cyanide. The experiments were made with a stationary electrode and a rotating electrode in series, with a copper coulometer. The runs lasted for one hour and the current density was 5 amperes per square decimeter. The solution, which was red at the start, became dark red in the case of the stationary electrode, and nickel hydroxide or cyanide precipitated. In the case of the rotating cathode, the solution changed from a red to a lemon yellow and yielded less of the green precipitate than the stationary one. The efficiency of deposition from this solution is very low and has been found by Watts as 0.05 percent. This is due to the very low concentration of nickel ions in the solution. It would accordingly be expected that rotation of the cathode would increase the efficiency over that of the stationary electrode.

The results obtained are tabulated in the following table:

R, P. M.	Percentage Efficiency Rotating	Percentage Efficiency Stationary
500	0.13	0.033
500	0.13	0.048
1000	0.41	0.022
1000	0.58	0.000
2000	1.65	0.057

These values are shown in the curves in Figure 3. The efficiency increases with increased rotation according to the pre-

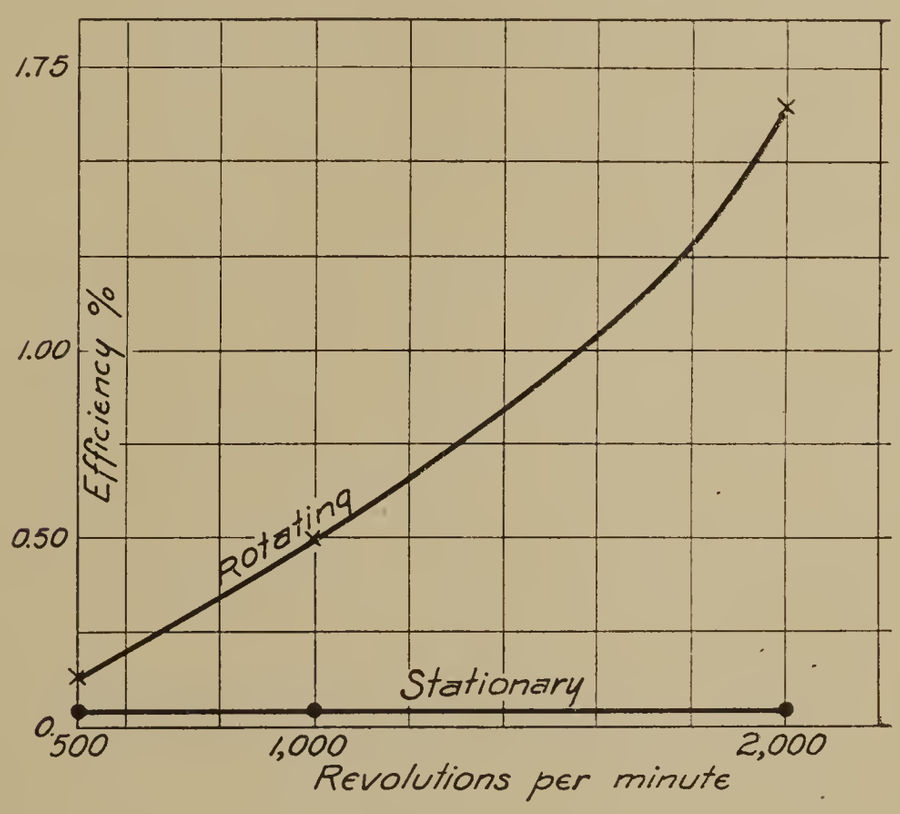

FIG. 3.

diction, and the efficiency of the rotating cathode is higher than that for the stationary.

In conclusion, it may be said that in the nickel ammonium sulphate solution the efficiency of the deposition of nickel on the rotating cathode, as well as on the stationary one, may be changed by changing the concentration of hydrogen ions. When the concentration of hydrogen ions is practically zero, as in the case of a strongly alkaline solution, nickel is deposited more easily than the other ions, so that the lower efficiency would be occasioned by impoverishment of nickel. The rotation of the electrode pre-

vents this impoverishment, and therefore increases the efficiency, while in the case of solutions where hydrogen ions are precipitated, the rotation of the cathode tends to prevent hydrogen ion impoverishment and therefore tends to decrease the efficiency.

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ELECTROCHEMICAL SYNTHESIS OF PHENYLHYDROXYLAMINE

By F. M. Frederiksen.

Snowdon[1] has pointed out that the chemical and electrochemical methods of reducing nitrobenzene are by no means similar though, in general, they should be. At the suggestion of Professor Bancroft, I have made a few experiments to fill one gap in the case of phenylhydroxylamine. Bamberger[2] prepared phenylhydroxylamine chemically by heating nitrobenzene for a few minutes with zinc dust and water. The yield varies very much—from 0 to 57 percent of the theoretical. Bamberger calls attention to the fact that different samples of zinc dust give very different yields even though the content of metallic zinc be the same and even though all other conditions are kept the same. Thus, one sample of zinc dust gave aniline and no phenylhydroxylamine. Bamberger considers that these enormous differences may be due in part to the fact that one sample of zinc dust gives chiefly molecular and therefore inactive hydrogen. Another way of wording the same thing is to say that different impurities in the zinc affect the over-voltage differently. The best yield was obtained by adding ten grams of nitrobenzene to half a liter of boiling water, throwing in 75 g. zinc dust (about 67 percent metallic zinc) all at once, boiling for three-quarters of an hour, cooling rapidly and saturating with sodium chloride. The phenylhydroxylamine was shaken out with ether, the ether distilled off, and the crystallized oil washed with ligroin. The yield was 57 percent of the theoretical. Other products are azoxybenzene, azobenzene, and aniline.

The question of yield is also discussed by Wohl[3], who had discovered the reaction independently of Bamberger. At first, nitro-

[1] Jour. Phys. Chem., **15**, 797 (1911).
[2] Ber. deutsch. chem. Ges., **27**, 1348, 1548 (1894).
[3] *Ibid.*, **27**, 1432 (1894).

benzene was heated for twenty minutes with ten times its volume of water and an excess of zinc dust. With 50 percent of zinc dust a yield of about 12 percent phenylhydroxylamine was obtained. When three times the theoretical amount of zinc was taken, the yield increased to about 20 percent. It is not feasible to heat for a long period because azoxybenzene, azobenzene, and aniline are then formed.

It was found that salts like calcium chloride, magnesium chloride, and zinc chloride accelerate the reaction between zinc dust and nitrobenzene. According to Wohl, this is because they form insoluble salts with zinc hydroxide. To obtain the best yield 250 c.c. 60 percent aqueous alcohol was heated in a flask with reverse cooler. To the flask was added 60 g. nitrobenzene and then 6 g. anhydrous calcium chloride, after which 75 g. commercial zinc dust was added in the course of fifteen minutes. The contents of the flask were heated for about five minutes after the last of the zinc dust was added, and were then cooled and filtered. The alcohol was distilled rapidly from the filtrate until an oil layer appeared which solidified on cooling. About 70-75 percent of the theoretical yield of phenylhydroxylamine was obtained in this way[4].

Wislicenus and Kaufmann[5] found that a 38 percent yield of phenylhydroxylamine could be obtained by reducing nitrobenzene in 90 percent alcohol with amalgamated aluminum. In a later paper Wislicenus[6] points out that better results are obtained with an ether solution. Nitrobenzene is dissolved in at least ten times its volume of ether, freshly prepared amalgamated aluminum is added and then water, a little at a time. The flask is equipped with a reverse cooler and is placed in ice to prevent the ether from foaming too much. When one starts with 20-30 g. nitrobenzene the yield of phenylhydroxylamine is said to be quantitative.

Bamberger and Knecht[7] obtained an 85 percent yield of phenylhydroxylamine (3.8 g.) by dissolving 5 g. nitrobenzene in 50 c.c.

[4] Bamberger states that he has never been able to average more than 35 percent yield in this way and that the maximum observed was 50 percent. Ber. deutsch. chem. Ges., **29**, 864 (1896).

[5] Ber. deutsch. chem. Ges., **28**, 1326, 1983 (1895).

[6] *Ibid.*, **29**, 494 (1896).

[7] *Ibid.*, **29**, 863 (1896).

90 percent alcohol and adding, first a solution of 12 g. aluminum sulphate in 100 g. water, and then 250 g. of a 5 percent zinc amalgam. The mixture was shaken vigorously for two hours, the temperature being kept below 5°.

I repeated Wohl's work, heating 250 c.c. of 60 percent alcohol with 60 g. nitrobenzene and 6 g. $CaCl_2$ (ammonium chloride is just as good) on a water-bath in a flask equipped with a return condenser. After bringing the solution just to boiling, 95 g. zinc dust was added through an interval of fifteen minutes, the temperature of the water bath being regulated so that the liquid in the flask boiled gently while the reaction was taking place. Five minutes after all the zinc dust had been added the reaction mixture was cooled, first with running water and then with ice. The mixture was filtered by suction and the zinc oxide washed with about 50 c.c. alcohol. The alcohol was boiled off until the temperature of the distilling vapor reached 86°, this being about the point at which the solution clouds owing to the separation of an oil. When the solution is cooled in a freezing mixture, the phenylhydroxylamine separates in crystals contaminated with some azobenzene. The crystalline mass, colored a bright orange by the azobenzene, was filtered by suction and then washed with ligroin. The washing must be done with care because phenylhydroxylamine is somewhat soluble in ligroin. The azobenzene is removed practically completely, leaving the phenylhydroxylamine almost pure and white. The yields varied between 30 and 40 percent, which is in accord with the results of Bamberger[8].

An attempt was now made to duplicate the reaction electrolytically by using zinc electrodes in an ammonium chloride solution. Of course a zinc anode is not essential theoretically; but it obviates the use of a diaphragm and cuts down the voltage considerably. Since it would be difficult to use electrodes having a surface equal to, say, 100 g. zinc dust, the reaction must take longer. In order to prevent the decomposition of the phenylhydroxylamine, which would probably occur if the solution were kept heated a long time, it was deemed advisable to run at a low temperature.

[8] Ber. deutsch. chem. Ges., 29, 864 (1896).

The solution was placed in a 300 c.c. beaker and stirred during electrolysis by means of a spiral stirring rod run by a motor. After the reduction had gone on as long as desired, the solution was filtered through a Büchner by suction and the alcohol then distilled off as in the chemical reduction. On account of the smaller amounts of substance taken, the solution was not cooled and filtered, but was saturated with sodium chloride and extracted with ether. The ethereal extract contained the phenylhydroxylamine and azobenzene with only a trace of salt or of ammonium chloride. The ether was driven off and the residue was crystallized from a small amount of benzene to which ligroin was added after solution and filtration. Phenylhydroxylamine is very soluble in hot benzene and only slightly soluble in cold benzene. Addition to the benzene of an approximately equal volume of ligroin cuts down the solubility a great deal. The azobenzene remains in solution.

Theoretically it requires 107.2 ampere hours (4 x 26.8) to reduce one molecular weight of nitrobenzene (123 g.) to phenylhydroxylamine. Since nitrobenzene has a specific gravity of 1.2, 10 c.c. nitrobenzene is approximately 12 grams and calls for 10.46 ampere hours, which should give 10.73 grams phenylhydroxylamine.

The following results were obtained:

Run 1: 250 c.c. 60 percent alcohol, 12.5 g. ammonium chloride, 10 c.c. nitrobenzene. Zinc electrodes. Cell packed in ice. Average temperature 12°. One ampere for 9.5 hours. No stirring for the first hour. Yield, 28 percent.

Run 2: 250 c.c. 60 percent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled in running water. Average temperature 14°. 0.75 ampere for 6.7 hours. Yield, 21 percent.

Run 3: 250 c.c. 60 percent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled in freezing mixture. Average temperature —5°. 0.75 ampere for 6.7 hours. Yield, 20 percent.

Run 4: 250 c.c. 60 percent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell cooled with running water. Average temperature 19°. 2 amperes for 2.67 hours. Yield, 29 percent.

Run 5: 250 c.c. 60 percent alcohol, 10 g. ammonium chloride, 5 c.c. nitrobenzene. Zinc electrodes. Cell not cooled. Average temperature, 36°C. 4.8 amperes for 1.11 hours. Yield, 22 percent.

These yields are all lower than those for the chemical reduction; but part of this difference is undoubtedly due to the fact that the losses are greater when 6 g. nitrobenzene is used instead of 60 g. in the same amount of solution. Also, we do not know what the reduction efficiency of the zinc dust is, though that could be determined; but we know that it is necessary to use more than the theoretical amount of zinc. The time at my disposal did not permit me to make runs to see what effect an excess of ampere hours would have.

It is possible to tell something about the results during the run. If much hydrogen is evolved at the cathode or if much zinc is precipitated there, the efficiency is necessarily low. A deep red color to the solution shows a considerable formation of azobenzene, an orange color a much less formation, and a light yellow color hardly any formation of azobenzene.

GENERAL CONCLUSIONS.

1. It is possible to reduce nitrobenzene to phenylhydroxylamine electrochemically without the use of a diaphragm, by using a zinc anode.

2. The chemical process of reducing nitrobenzene to phenylhydroxylamine with zinc dust can be duplicated electrochemically.

3. The yield from the electrochemical process is less at present than the yield from the chemical process. Part of this difference is due to the fact that the percentage losses are larger the smaller the amount of nitrobenzene taken.

4. The efficiency of reduction and the conversion to azobenzene both decrease with falling temperature. One has to strike a mean therefore between slight conversion to azobenzene but low

reduction efficiency, and high reduction efficiency with high conversion to azobenzene. The best results so far have been obtained at about room temperature.

I take this opportunity to express my appreciation of the active interest Professor Bancroft has taken in the progress of this work.

Cornell University.
Ithaca, N. Y.

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THE PEPTONIZATION OF CHROMIC OXIDE.

By Wilder D. Bancroft.

Fischer and Herz[1] point out that the addition of an excess of caustic soda or potash to a green solution of chromic chloride gives rise to a clear green solution, because the precipitated hydrous chromic oxide apparently dissolves in the excess of alkali. On long standing, the solution becomes cloudy through precipitation of hydrous chromic oxide. This precipitation takes place more slowly the greater the excess of alkali. It takes place more rapidly, the higher the temperature. These facts, together with the difficulty of redissolving the chromic oxide in alkali caused Fischer and Herz to suspect that the apparent dissolving of chromic oxide in caustic alkali was really a peptonization. On that assumption no alkaline chromite is formed.

Fischer and Herz made dialysis experiments and conductivity experiments to confirm this hypothesis. "An alkaline solution of chromic hydroxide was prepared by adding an excess of caustic soda to a chromic chloride solution. This was dialyzed against pure water using animal bladder as a membrane. All the experiments showed that the water outside soon became alkaline but remained colorless for several days. A heavy precipitate of chromic hydroxide formed on the membrane. The alkaline solution of chromic hydroxide thus behaves like a typical colloid as opposed to a similar solution of aluminum hydroxide in caustic soda which contains a true compound, the aluminum diffusing perceptibly through the membrane. . . .

"As a further confirmation of the view that chromic hydroxide is peptonized by caustic solutions, measurements of the electrical conductance were made, the underlying idea being that the electrical conductance of a solution of chromic hydroxide in caustic soda must depend on the caustic soda if the chromic

[1] Zeit. anorg. Chem., **31**, 352 (1902).

hydroxide is in colloidal suspension. The precipitation of the chromic hydroxide can only affect the conductance slightly. If a compound is formed, the precipitation of the chromic hydroxide involves a decomposition of the dissolved and conducting compound and must therefore cause a change in the conductance. Since the precipitation of chromic hydroxide from a caustic soda solution can easily be brought about by boiling, the experiments were carried out in the following way:

"To a solution of green chromic chloride sufficient caustic soda was added to dissolve the precipitate first formed. The electrical conductance of this solution was then determined. The solution was heated and the precipitated chromic hydroxide filtered off. The conductance of the filtrate was determined and it was found that heating and filtering had not changed the conductance. . . . From these experiments it follows with great probability that a colloidal solution is formed when chromic hydroxide dissolves in caustic soda, whereas alumina forms a compound under similar conditions. Zinc hydroxide seems to be an intermediate case, being present in alkaline solutions partly as zincate and partly in colloidal form.

"If these experiments are repeated, starting with chromic sulphate solution instead of with chromic chloride solution, there seems to be complications which are probably due to the formation of chrome sulphuric acids and which have not been studied in detail."

While Fischer and Herz are undoubtedly right in their conclusion, some details of their experiments are not above criticism. In the first place it is not correct theoretically to say that the precipitation of the hydrous chromic oxide will have no effect on the conductivity of the solution. In so far as the hydrous chromic oxide is peptonized by hydroxyl ions, the adsorption of these ions must produce some change in the conductivity. When the hydrous chromic oxide precipitates, it carries down with it an indefinite amount of water and of alkali, which must also have an effect. It is possible, of course, that the removal of the alkali is counterbalanced practically by the removal of the water; but that can only be a coincidence and cannot be true generally. What is more likely is that the change of conductivity fell within the limit of experimental error, since there

was present a large excess of caustic soda. One would have felt more confidence in the unpublished data if Fischer and Herz had not obtained results which agreed admirably with their faulty theoretical conclusions. It seems desirable therefore to confirm their results by other experiments and this has been done for me by Mr. Nagel.[2]

Fischer and Herz state that an alkaline solution of hydrous chromic oxide becomes turbid on standing, owing to the precipitation of the oxide and that this precipitation takes place more slowly the greater the excess of caustic alkali; but they do not say how great the precipitation is, apparently because they were more interested in the fact that practically complete precipitation can be obtained in a short time by heating the solution. Mr. Nagel treated freshly precipitated hydrous chromic oxide with an excess of caustic potash to prevent jelling, and set the solutions away in glass-stoppered bottles. At the end of three weeks a large amount of green precipitate had formed, but the liquid was still green. At the end of two months the solution was only faintly yellowish green, the bulk of the chromium oxide having precipitated. There is therefore a slow agglomeration and precipitation of the peptonized oxide, the rate of agglomeration being cut down by the excess of the peptonizing agent, the hydroxyl ions.

Filtration experiments have also been made, using a Bechhold ultra-filtration apparatus[3] and collodion filters. The hydrous chromic oxide is filtered out completely from an alkaline solution, the filtrate coming through colorless. While there may be some adsorption by the filter, this is of no importance because the filtration was carried on until hydrous chromic oxide was left in mass on top of the collodion filter and could be scraped off from it. Chromic chloride solution, on the other hand, runs through green, the dissolved salt not being removed.

This raised the question as to what one has in a so-called basic chromic solution. When hydrous chromic oxide is heated with a chromic chloride solution, some of the chromic oxide seems to go into solution. With an ultra-filter the chromic chloride solution passes through, while the hydrous chromic oxide is

[2] Jour. Phys. Chem., **19**, 569 (1915).
[3] Bechhold: Zeit. phys. Chem., **60**, 257 (1907); 64, 328 (1908).

filtered out. It is therefore clear that a so-called basic chromic chloride solution contains hydrous chromic oxide peptonized, but not dissolved, by chromic chloride. There is no evidence that any appreciable amount of basic salt is formed in solution, though no quantitative measurements have been made in regard to this.

Mr. Nagel also tried to shake out peptonized chromic oxide with benzene or kerosene, but this proved impossible in alkaline solutions. When precipitated chromic oxide is shaken with water and benzene, it goes into the dineric interface;[4] but addition of caustic alkali causes it to precipitate, presumably because the alkali is itself adsorbed by the organic liquid.[5]

Fischer and Herz[6] state that an alkali chloride has very little effect in precipitating hydrous chromic oxide peptonized by caustic soda, but that it has a marked effect in precipitating hydrous chromic oxide peptonized by barium hydroxide. This is undoubtedly due to the fact that the bivalent barium ions are adsorbed more strongly than the univalent sodium ions and consequently make the peptonized oxide more nearly neutral and less stable. I should expect to find that barium hydroxide has a lesser peptonizing action than caustic soda. This experiment was not tried by Fischer and Herz; but they showed that caustic potash has a greater peptonizing action than caustic soda, which proves that the concentration of hydroxyl as ion is not the sole factor in peptonization. In line with this is the fact that hydrous chromic oxide peptonizes hydrous ferric oxide and is carried down by it.[7]

GENERAL CONCLUSIONS.

1. Using a collodion ultra-filter it is possible to filter out the hydrous chromic oxide peptonized by caustic alkali.

2. On long standing, nearly all of the peptonized chromic oxide precipitates from a caustic alkali solution.

3. Chromic chloride solutions peptonize hydrous chromic oxide. No appreciable amount of basic chloride appears to be formed.

4. It is not possible to shake out hydrous chromic oxide from

[4] Bancroft: Jour. Phys. Chem., **19**, 275 (1915).

[5] Wilson: Jour. Chem. Soc., **1**, 174 (1848); Twomey: Jour. Phys. Chem., **19**, 360 (1915).

[6] Zeit. anorg. Chem., **31**, 355 (1902).

[7] Nagel: Jour. Phys. Chem., **19**, 331 (1915).

an alkaline solution either with benzene or kerosene, even though benzene will remove hydrous chromic oxide from water.

5. Since hydroxyl ions are the active peptonizing agents with hydrous chromic oxide, a strongly adsorbed cation will decrease the stability of the colloidal solution.

5. The order of decreasing stability is potassium, sodium, barium, iron.

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DISCUSSION.

L. H. Duschak: Prof. Hildebrand, of the University of California, told me a few days ago that he hoped to be present to discuss this paper, as some recent experiments of his are of interest in this connection. Since he is not here, I will briefly outline his results.

By using the familiar arrangement of hydrogen electrode (Hildebrand, J. Am. Chem. Soc. (1913) **35**, 847) in conjunction with a calomel electrode it is possible to follow with considerable accuracy small changes in the hydrogen ion concentration in a solution such as occur when a weak acid is being neutralized by an alkali. Thus, in the case of freshly precipitated aluminum hydroxide (*loc. cit.* p. 863) in suspension, if the potential of the hydrogen electrode is plotted as a function of the alkali added, a curve will be obtained showing a distinct break when, using sodium hydroxide for example, sufficient alkali has been added to form the compound $NaAlO_2$ at which point the re-solution of the aluminum hydroxide appears to be complete. In other words, there is a distinct disappearance of hydroxide ion until this reaction is complete, after which the increase in hydroxide ion concentration corresponds to the further additions of alkali. This behavior constitutes strong evidence of the formation of a definite chemical compound when aluminum hydroxide is dissolved by an alkali.

Prof. Hildebrand has recently performed this same experiment with chromic hydroxide. In this case, however, not only is the

definite break in the curve corresponding to the formation of such a compound as $NaCrO_2$ lacking, but the course of the curve beyond the point where such a break might be looked for indicates the continued disappearance of hydroxide ions, as the addition of alkali is continued. There is therefore no evidence that chromic hydroxide plays the part of an acid when appearing to dissolve in alkali. The gradual removal of hydroxide ions from solution may be explained as an adsorption phenomenon, thus confirming the view taken by Prof. Bancroft of the behavior of chromic hydroxide in alkaline solution.

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ELECTROMOTIVE FORCES.

By Wilder D. Bancroft.

The present theory of the electromotive force of the voltaic cell is due primarily to Nernst[1] and consequently the subject is usually presented in text-books in the form adopted by Nernst, with subsequent modifications to meet special cases. It so happens that the historical development is not a logical or a consistent one; and consequently the different types of cells are not co-ordinated as they should be.

If we have a reversible electrode such as zinc in zinc sulphate, we make use of Nernst's deduction and write for the single potential

$$E = \frac{RT}{nF} \log \frac{P_{Zn}}{p} \tag{1}$$

where P_{Zn} is the hypothetical solution pressure of zinc, p the osmotic pressure of zinc in the solution, n the valence of the zinc ions and F the Faraday constant.

If we make up a cell of two different concentrations of zinc sulphate we write for it the equation

$$E = \frac{RT}{nF}\left\{\log \frac{P_{Zn}}{p_d} - \log \frac{P_{Zn}}{p_c}\right\} + x = \frac{RT}{nF} \log \frac{p_c}{p_d} + x \tag{2}$$

where x is the potential difference between the two solutions, p_c is the more concentrated solution and p_d the more dilute. If we make up a cell of the Daniell type, the equation becomes

$$E = \frac{RT}{nF}\left\{\log \frac{P_{Zn}}{p_{Zn}} - \log \frac{P_{Cu}}{p_{Cu}}\right\} + x = \frac{RT}{nF} \log \frac{P_{Zn}}{P_{Cu}} \cdot \frac{p_{Cu}}{p_{Zn}} + x \tag{3}$$

[1] Zeit. phys. Chem., 4, 129 (1889).

If the metallic electrode is a phase of varying composition such as a dilute amalgam, it is usual to consider the cell as a whole and to calculate the work done in transferring the dissolved metal from one electrode to the other as pointed out by von Turin[2] and by Meyer.[3] The equation for the cell is

$$E = \frac{RT}{mnF} \log \frac{p'_1}{p'_2} \tag{4}$$

Where p'_1 and p'_2 are the osmotic pressures of the metal in the two mercury solutions and m is the ratio of the molecular weight of the metal in the mercury solutions to the weight of the ion in solution. LeBlanc[4] writes for the single potential

$$E = \frac{RT}{nF} \log \frac{P'}{p} \tag{5}$$

Where P' is the electrolytic solution pressure of the zinc in the amalgam and m is unity because zinc is monatomic in mercury. This solution pressure is not the one introduced by Nernst because that was a constant. As a matter of fact, LeBlanc gets out of the difficulty only by saying that since the osmotic pressures of zinc in mercury are proportional to the concentrations, the electrolytic solution pressures of the amalgams may be assumed to be proportional to the osmotic pressures of the dissolved zinc. In a cell with two amalgam electrodes the proportionality factor cancels and everything comes out as it should; but it would be a very clever student who could find out from LeBlanc's book the equation for a cell consisting of zinc and dilute zinc amalgam in zinc sulphate solution. If we assume that the apparent solution pressure is proportional to the osmotic pressure of the monatomic metal in the mercury, the equation for the single potential becomes

$$E = \frac{RT}{nF} \log \frac{P_{Zn}}{p_0} \cdot \frac{p'_1}{p} \tag{6}$$

where P_{Zn} is the solution pressure of zinc against an aqueous solution as in Equation 1, p'_1 is the osmotic pressure of zinc in

[2] Zeit. phys. Chem., **5**, 340 (1890); **7**, 221 (1891).
[3] Wied. Ann., **40**, 244 (1890); Zeit. phys. Chem., **7**, 477 (1891).
[4] A Text-Book of Electrochemistry, 184 (1907).

the amalgam, p_0 is the osmotic pressure of a solution of zinc in mercury which is in equilibrium with pure zinc, and p is the osmotic pressure of zinc ions in the solution.

When it comes to gas cells the orthodox thing is to treat them exactly like amalgam cells, only considering the solution pressures as proportional to the gas pressures. The equation for the single potential therefore becomes

$$E = \frac{RT}{mnF} \log \frac{p''_1}{p} \tag{7}$$

where p''_1 is the gas pressure. For hydrogen $m = 2$ and $n = 1$. We are not only ignoring the electrode but also the unknown concentration in the electrode. While this is justifiable thermodynamically, it is of doubtful wisdom pedagogically. We can get back to the strict Nernst formulation if we postulate Henry's law for the relation between the gas pressure and the unknown osmotic pressure in the electrode and substitute this in an equation analogous to Equation 6. If the ratio of the molecular weight of the gas to the molecular weight in the metal electrode is q, we have

$$E = \frac{RT}{qmnF} \log \frac{P}{Kp_0} \cdot \frac{p''_1}{p} \tag{8}$$

where K is the constant in the equation $p''_1 = K(p'_1)^q$ and p'_1 is the osmotic pressure of hydrogen in the electrode. For hydrogen we know that $qm = 2$. Since there is no concentration at ordinary temperatures for which solid hydrogen is in equilibrium with a platinum electrode, for instance, it is simpler to substitute P_1 for P/Kp_0 in which case we may write

$$E = \frac{RT}{2F} \log \frac{P_1 p''_1}{p} \tag{9}$$

remembering however that P_1 is not the solution pressure of solid hydrogen.

When it comes to oxidation and reduction cells, the Nernst formulation is practically ignored. For reversible electrodes such as platinum in a mixture of ferrous and ferric salts we follow

the lead of Peters[5] and write one modification of the van't Hoff formulation

$$E = A - \frac{RT}{nF} \log \frac{p_2}{p_1} \qquad (10)$$

where p_1 is the osmotic pressure of the ferrous ions in the solution, p_2 the osmotic pressure of the ferric ions, n the difference in valence of the ferric and ferrous ions ($n = 1$), and A the value of the electromotive force when p_1 and p_2 are equal.[6] While this same formula could probably have been deduced from the Nernst theory, I am not aware that it has ever been done. Nernst has suggested treating reduction electrodes as hydrogen electrodes; but it is not very satisfactory to call a ferric-ferrous electrode a hydrogen electrode, and the overvoltage complicates the theory of the hydrogen electrode a good deal.

When avowedly measuring chemical affinity, as involved in the reaction $TlSCN + KCl \leftrightharpoons TlCl + KSCN$ for instance, we make use of another modification of the van't Hoff formulation[7] and write for the cell

$$E = \frac{RT}{nF} \log \frac{Kp_1}{p_2} \qquad (11)$$

where p_1 is the osmotic pressure of the sulphocyanate ion, p_2 the osmotic pressure of the chloride ion, K is the equilibrium constant in the equation $Kp_1 = p_2$, and x is the potential difference between the solutions. The Nernst formulation could have been used in this case. Ostwald[8] has shown that the equation for such single potential differences as Tl | *TlSCN* KSCN may be written

$$E = \frac{RT}{nF} \log \frac{Pp_1}{S_1^2} \qquad (12)$$

where P is the solution pressure of thallium, p_1 the osmotic pressure of the sulphocyanate ions, and S_1 the solubility of thallous

[5] Zeit. phys. Chem., 26, 193 (1898).

[6] Peters uses the plus sign in his equation; but this is not in keeping with the Nernst formulation that the current flows from the metal to the solution when E is positive. See Haber: Zeit. Elektrochemie, 7, 1047 (1901).

[7] Knüpffer: Zeit. phys. Chem., 26, 255 (1898).

[8] Lehrbuch allgem. Chemie, 2 I, 877 (1893).

chloride expressed in osmotic pressure units. For the cell Tl | *TlSCN* KSCN | KCl *TlCl* | Tl we have the equation

$$E = \frac{RT}{nF}\left\{\log\frac{Pp_1}{S_1^2} - \log\frac{Pp_2}{S_2^2}\right\} = \frac{RT}{nF}\log\frac{S_2^2}{S_1^2}\cdot\frac{p_1}{p_2} \qquad (13)$$

provided we consider the potential difference between the solutions as zero.

I have distinguished five types of cells: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells. These are usually treated in five more or less different ways, which may be advantageous but which is certainly unsound theoretically. Suppose we take the Daniell cell, Zn | $ZnSO_4$ | $CuSO_4$ | Cu. This is usually considered—and very properly—as a cell with reversible metallic electrodes. It may however be considered as an oxidation and reduction cell because the zinc is oxidized and the copper salt is reduced.[9] It can also be considered as a case of chemical affinity because we are really studying the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4.$$

If we start with a zinc amalgam and a copper amalgam instead of with the pure metals, we have the same reaction taking place as before; but it is now an amalgam cell with electrodes of varying composition. If we were to take into account the unknown vapor pressures of zinc and copper, we could consider the cell as a gas cell. Our types are not mutually exclusive and one given combination may be considered from any one of the five differing points of view. Obviously it would be better for the student to have a uniform treatment of the subject and yet I do not know of any text-book on electrochemistry which attempts this. I am not in a position to do much criticizing because I have never attempted it myself in my lectures in the past, though I have pointed out the inter-relation of the different types.

The proper starting point, as Haber [10] has pointed out, is van't Hoff's formula for the reaction isotherm. In the case of

[9] Haber: Zeit. Elektrochemie, 7, 1046 (1901).
[10] Zeit. Elektrochemie, 7, 1045 (1901).

a reversible reaction A, the chemical affinity per unit chemical weight, is given by the equation

$$A = RT \log K \Sigma p_1 / \Sigma p_2 \tag{14}$$

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed. If it is possible to arrange the reaction so that electricity is generated, we have the relation

$$A = nFE \tag{15}$$

By combining Equations 14 and 15, we get the working equation

$$E = \frac{RT}{nF} \log K \Sigma p_1 / \Sigma p_2 \tag{16}$$

If we apply Equation 16 to the Daniell cell,

$$Zn \mid ZnSO_4 \mid CuSO_4 \mid Cu,$$

which involves the reaction

$$Zn + CuSO_4 = Cu + ZnSO_4,$$

we have

$$E = \frac{RT}{nF} \log K . Zn . p_{Cu} / Cu . p_{Zn} + x \tag{17}$$

where x represents the potential difference between the solutions and Zn and Cu are written to denote the unknown constant terms for zinc and copper respectively. By combining these latter with K we get

$$E = \frac{RT}{nF} \log K_1 p_{Cu} / p_{Zn} + x \tag{18}$$

which is identical with Equation 3, provided we put $K_1 = P_{Zn} / P_{Cu}$. The single potential difference at the zinc electrode can be written

$$E = \frac{RT}{nF} \log K' . Zn / p_{Zn} = \frac{RT}{nF} \log K_2 / p \tag{19}$$

which is the same as Equation 1 with K_2 written for P_{Zn}. The equation for a concentration cell with zinc electrodes and two zinc sulphate solutions becomes

$$E = \frac{RT}{nF} \log \frac{K_2}{K_2} \cdot \frac{p_1}{p_2} \tag{20}$$

which is the same as Equation 2, p_1 being the more concentrated solution. The direction of the current is to be predicted from the Theorem of Le Chatelier.

If the molecular weight of zinc in a zinc amalgam is m times the atomic weight of zinc the potential difference between it and the solution will be given by the equation

$$E = \frac{RT}{mnF} \log Kp'_1 / p \tag{21}$$

which is the same as Equation 6 with K written for P_{Zn}/p_0. The equation for an amalgam cell with electrodes of different concentrations becomes

$$E = \frac{RT}{mnF} \log \frac{Kp'_1}{Kp'_2} \cdot \frac{p}{p} = \frac{RT}{mnF} \log \frac{p'_1}{p'_2} \tag{22}$$

which is the same as Equation 4.

In the case of a gas electrode we can write at once

$$E = \frac{RT}{qmnF} \log Kp''_1 / p \tag{23}$$

where qmn is the ratio of the molecular weight of the gas to the ionic weight, p''_1 is the gas pressure and p is the osmotic pressure of the ion for which the electrode is reversible. In the case of hydrogen or chlorine $qmn = 2$. Equation 23 is the same as Equation 9 if $K = P_1$.

The equation for a reversible reduction electrode consisting of platinum in a mixture of ferrous and ferric salts becomes

$$E = \frac{RT}{nF} \log Kp_1 / p_2 \tag{24}$$

where p_1 refers to the ferrous salt and p_2 to the ferric salt. This is the same as Equation 10 when one writes $A = (RT/nF)\log K$.

I have already shown that the equation for the Daniell cell simplifies to

$$E = \frac{RT}{nF} \log K_1 p_{Cu} / p_{Zn} + x \tag{18}$$

whether we consider the cell as a case of chemical affinity or as made up of two reversible electrodes. For the cell Tl | *TlSCN* KSCN KCl | *TlCl* | Tl the reaction is

$$TlSCN + KCl \leftrightharpoons TlCl + KSCN.$$

Considering this as a case of chemical affinity and combining the constant terms for thallous chloride and thallous sulphocyanate with the equilibrium constant we get

$$E = \frac{RT}{nF} \log K_1 \, p_{SCN} / p_{Cl} + x \qquad (25)$$

which is identical with Equation 11.

It is possible to apply the general equation of van't Hoff to the contact electromotive force between two solutions, in case the process is a reversible one.[11] For the same electrolyte in different concentrations, Nernst has derived the expression

$$E = \frac{u - v}{u + v} \cdot \frac{RT}{nF} \log \frac{p_1}{p_2} \qquad (26)$$

where the valence n of the ions is the same, p_1 and p_2 are the osmotic pressures of the ions in the concentrated and dilute solutions, respectively, and u and v refer to the ionic mobilities.

One may imagine the potential difference between two solutions of hydrochloric acid to be produced by two opposing tendencies, one of these being the diffusion of hydrogen ions into the dilute solution and the other being the diffusion of chlorine ions in the same direction. If the rates of ionic diffusion are equal no boundary electromotive force is produced.

Consider separately the part played by the hydrogen ions. Since the ion concentrations in the two solutions are equal when equilibrium is reached, K in the van't Hoff formula becomes unity and disappears. The substance consumed is the ionic hydrogen in the concentrated solution and Σp_1, refers to its osmotic pressure; similarly Σp_2 refers to the dilute solution where hydrogen ions are increasing in number. If the total EMF were produced by the migration of hydrogen ions only, the following expression would hold for this hypothetical single potential:

[11] This was pointed out to me by Professor Briggs, who has written this section for me.

$$E_1 = k_1 \frac{RT}{nF} \log \frac{p_1}{p_2} \tag{27}$$

where k_1 is a constant proportional to the relative rate of ionic diffusion.

On the other hand, negatively charged chlorine ions are passing from the concentrated into the dilute solution. Considering the chlorine ions separately, the hypothetical single potential would be:

$$E_2 = -k_2 \frac{RT}{nF} \log \frac{p_3}{p_4} \tag{28}$$

where p_3 is the osmotic pressure of the chlorine ions in the concentrated solution, p_4 refers to the dilute solution and k_2 is a constant proportional to the relative ionic mobility of the chlorine ions.

Actually, therefore, the contact potential is equal to the sum of the effects due to the cation and anion and, since $p_1 = p_3$ and $p_2 = p_4$, we may combine Equations (27) and (28) into the following:

$$E = E_1 + E_2 = (k_1 - k_2) \frac{RT}{nF} \log \frac{p_1}{p_2} \tag{29}$$

If we substitute $\frac{u}{u + v}$ for k_1 and $\frac{v}{u + v}$ for k_2, Equation 26, the Nernst equation, is obtained.

I have tried to make clear that all the different types of reversible cells which have been discussed can be treated from one point of view if one makes use of the van't Hoff formula given in Equation 16. This is, in my opinion, a much better way of treating the subject than the ordinary, haphazard and illogical method. On the other hand this treatment ignores the historical development and fails absolutely to bring out the important part played by Nernst. It seems to me that the following compromise ought to be fairly satisfactory both to the historical and the logical enthusiasts. Present Nernst's deduction of the potential difference between solutions. This would also include Planck's modification of Nernst's formula,[12] and later work along this line.

Then take up Nernst's formula for the potential difference

[12] Planck: Wied. Ann., 39, 161; 40, 561 (1890).

between a metal and a solution, applying it to concentration cells, to the Clark cell, and to the Daniell cell, much as Nernst has done; but introducing at once Ostwald's explanation of electrodes of the second class. Next, deduce the van't Hoff formula, Equation 16, and apply it to the cases already studied, after which one should take up in order the so-called chemical affinity cells, the oxidation and reduction cells, the amalgam cells, and the gas cells. It is usual, I know, to discuss gas cells before oxidation and reduction cells, but I think that this is another case of a too slavish following of the historical development. It is certainly more logical to study first the effect of varying concentration in the solution, then the effect of varying concentration in the electrode, and lastly the effect of varying concentration in the vapor phase. Certainly nobody can question the advantage of having studied the relation between chemical affinity and electromotive force before taking up the case of the hydrogen-oxygen gas cell.

The general results of this paper are:

1. Five types of reversible cells have been recognized. which are usually treated in five, more or less, different ways, even though a particular cell could be classed under any one of the five types.

2. The five so-called types of cells are: cells with reversible metallic electrodes; amalgam cells; gas cells; oxidation and reduction cells; chemical affinity cells.

3. All these cells can be treated from the same point of view provided one starts with the van't Hoff formula

$$E = \frac{RT}{nF} \log K\Sigma p_1 / \Sigma p_2,$$

where Σp_1 refers to the substances which are consumed during the reaction and Σp_2 to the substances which are formed.

4. It has been shown how the van't Hoff formula is to be applied in the special cases.

5. Since a consistent logical development of the theory of the electromotive force of voltaic cells does not do justice to the pioneer work of Nernst, a compromise treatment is suggested.

6. It is suggested that Nernst's work be presented as an historical introduction, after which the van't Hoff equation should be deduced and applied to all cases.

7. It is desirable to study, in order, the effect of varying concentration in the solution, in the electrode, and in the vapor. Consequently the amalgam cells should be considered after the oxidation and reduction cells, and before the gas cells.

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DISCUSSION.

PRESIDENT L. ADDICKS: This paper is not so formidable as one might think in looking at its mathematical appearance. It is a pedagogical question rather than a mathematical one, as to whether the student should be given the general discussion of the mathematical derivation of the voltage of the battery in the order in which it was developed by Nernst and others, or in the order in which he can understand it. That is, whether credit to the pioneer work should be sacrificed, or should it be given to the student as he can best grasp it. It seems to me as if he should get it as he can best grasp it.

MERLE RANDALL: On account of the importance of those reactions which occur in a voltaic cell during the passage of a current it is very desirable that suitable conventions be adopted for the sign of an electromotive force or of a single potential difference. From a practical standpoint it is likewise important to define the unit states or concentrations of the substances entering into, or formed in the reaction. In making the calculations which Professor Lewis and I (J. Am. Chem. Soc. (1914), **36**, 1969, 2259) have undertaken upon the free energy of chemical substances, we have found it very difficult to interpret the results of e.m.f. measurements, because little or no attention has been given to signs and units. It is to be regretted that the formulation of the author does not obviate these difficulties.

Lewis (J. Am. Chem. Soc. (1915), **35**, 20) has proposed a method of treatment of electromotive forces which is general, and which, moreover, does not involve the use of the hypothetical solution pressure or of the osmotic pressure of the ions. Not only may the same formulation be applied to any of the types of cell described by the author, but a system of notation is proposed which is at the same time simple and unambiguous.

Liquid potentials must, of course, be eliminated. The potential between solutions of the same electrolyte at two different concentrations may be calculated by Equation 26. The potential between equally concentrated solutions of two binary salts having one ion in common may be calculated by the formula of Lewis and Sargent (J. Am. Chem. Soc. (1909), **31**, 363).

$$E = RT/F \ln \lambda_1/\lambda_2$$

in which λ_1 and λ_2 are the equivalent conductivities of the two salts at the given concentration.

We are attempting a general revision of the table of single-electrode potentials, which with the tables of free energies promises greatly to facilitate the study of chemical affinity.

I certainly think with Professor Bancroft that the use of the so-called theoretical deductions of the electromotive force with the help of hypothetical solution pressure, osmotic pressure of the ions, and other "aids" is more confusing than helpful. It was always so to me. It is only since I have thrown away these methods and adopted the modification of the van't Hoff formula that I have had confidence in the use and interpretation of e.m.f. measurements.

Secretary J. W. Richards: I wish to say "Amen" to the sentiments which Mr. Randall has expressed, and to celebrate the decease of the hypothetical solution-pressure of the metals as a basis of calculating the electromotive force of batteries. I once had a delightful trip across the ocean on the same steamer with Professor van't Hoff and had some most interesting talks with him. He went at fundamentals in a very broad way, and I must admit that the van't Hoff formula, as stated here in conclusion three, is a manner of approach to the theory of the voltaic battery which appeals strongly to me. It simply considers the

substances consumed, and those which are formed. The idea which based the electromotive force of the battery upon the hypothetical pressure of solution of the metal, seemed to be working around in a circle. It always seemed to me that the solution-pressures of the metals carried on their own faces their own epitaph. They were impossible on first sight; not only hypothetical, but impossible figures. If we consider that the solution-pressures of the metals are supposed to vary from one one-millionth of an atmosphere up to several millions of atmospheres, some are negative and some positive, it seems simply impossible and ridiculous. They are merely figments of the imagination, calculated backwards so as to satisfy the conditions of a theory. I am glad to join in the funeral procession today.

C. J. Reed: I am very glad to hear Doctor Richards take the stand he does. It agrees with what I have always thought on the subject, that is, the electromotive force and the current being factors of the energy evolved, the energy of any chemical reaction is the only thing which can be used finally to determine the electromotive force. The current is fixed by Faraday's law of electrochemical equivalnts. Consequently, the electromotive force is proportional to the energy evolved in the reaction. The electromotive force must vary with the temperature on account of the chemical energy varying with the temperature. For instance, the energy evolved by a chemical reaction which takes place at red heat is not the same as the energy evolved in a reaction taking place at some other temperature. The combination of two elements at the temperature at which they would become dissociated would not evolve any energy because the energy absorbed in dissociation is equal to that evolved in combination.

L. H. Duschak: While I do not want to apply first-aid methods to this idea of solution pressure, it seems to me that the conception has been a useful one. Even in purely theoretical work it has been my experience that it is much easier to deal with the problems when one can form a physical picture of the process under consideration. A metal reacting with the solution possesses some intrinsic property independent of the nature of the solution, just as the vapor pressure of a substance is in general independent of the gases which surround it. So it seems to me that the idea

of solution pressure is a good one, even though, when studying the process thermo-dynamically, we express this property of the metal as a chemical potential or the equivalent.

President L. Addicks: I suppose, from a purely practical viewpoint, we can learn more from a volt-meter than we can with the calculus.

Merle Randall: With reference to the tables of free energy mentioned in my previous discussion, it is very likely that within the next ten years we will be able to refer to the table of free energies, or chemical affinities, and from that table determine the equilibrium in nearly every reaction with little more trouble than we, at present, obtain the heat of a reaction. Knowing the free energy of the reaction, we get from it the equilibrium. We have already tables for most of the non-metallic compounds of oxygen, hydrogen, carbon, iodine and nitrogen.

Secretary J. W. Richards: Referring to what Mr. Duschak said, pedagogically I would prefer not to teach a subject to students from the standpoint of a principle which I did not think was sound. It may be attractive to think of vapor pressure, and you can calculate a vapor pressure which would give any observed electromotive force. But I should prefer to give the students a general, over-all, broad standpoint, and carefully avoid a questionable standpoint as a basis. They too easily get an idea that it is true, and thereafter think in those terms. They quickly make realities out of what you put to them as hypotheses.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

USE OF THE FLAME ARC IN PAINT AND DYE TESTING.

By Wm. Roy Mott.

OUTLINE OF PAPER.

A. Introduction.
B. General Factors.
C. Testing in Sunlight.
D. The 5000 M. S. C. P. White-Flame Arc.
E. General Notes on Lamps Available.
F. Light of Different Flame Carbons.
G. Test Arrangements.
H. Comparison of Action of Sunlight and White-Flame Arc.
I. Action on Paints.
J. Conclusions.
K. Brief Summary of Literature.

A. Introduction.

The white-flame arc at 25 amperes affords light at two feet (60 cm.) distance more intense than summer sunlight; and unlike sunlight, this white light is exactly reproducible and available twenty-four hours in every day. Sunlight varies continually, due to shifting solar position and changing atmospheric conditions. Dyes and paints have been generally tested in sunlight because until the invention of the high amperage white-flame arc, sunlight was the most intense light practically available. Some good work has been done with the pure carbon arc (Ref. 3, 23) and with the quartz mercury arc (Ref. 23, 24, 60); but these are limited in value, the first by low intensity and the second by the source of the action being ultraviolet light, which is often different from the action of ordinary light. The high amperage white-flame arc has forced out all other forms of illumination as the cheapest, most powerful light source for photo-engraving. It is taking its legitimate place for blue-printing, for photographic studio work, and for laboratory and industrial manufacture of chemicals by light. The writer has made several hundred com-

parisons of the action of sunlight and of white-flame arc light on dyed fabrics and on paints and feels that sufficient has been done to invite a general consideration of this light in dye and paint investigations. There are great possibilities of new apparatus, of new fields and of a re-survey of the general field under definite, reproducible and efficient conditions. A brief summary of the literature given at the end of this paper shows much that needs to be investigated under conditions so arranged that anyone can repeat the experiments.

B. General Factors.

The action of light on dyes may take the following courses: (1) Fading without other color change, (2) Darkening before fading, (3) Change to a different color tint, and (4) composite effect as to depth into cloth, so that on viewing underhand (overhead) the cloth is darkened and on viewing overhand (at an angle) the cloth appears faded. The fastness of dyes may run through extremes of fading in a few hours in sunlight to lasting several months. Graded steps of exposure are necessary to follow the results, which are often complex combinations. There are six major factors affecting the action of light. These are: (1) Kind and intensity of light, (2) Atmosphere, (3) Dye, (4) Fiber, (5) Mode of applying dye, including mordants, fillers, etc., and, in paints, nature of oil and varnish medium, (6) Temperature. In the summary of the literature, several references to each of these factors are to be found.

(1) *Kind and Intensity of Light:* (Ref. 2, 4, 49.) The light has the least action when of the same color as the dye, due to the first law of conservation of energy, that the energy reflected cannot do chemical work. The complementary color (light absorbed), as pointed out by Bancroft and others, has the most action. In case of absorption of blue and other rays (red or green) there is generally more effect with the blue rays than with red or green. The effect of intensity of light is such in some cases as to entirely change the reaction. Even in simple cases the curve changes through three or four types of equations. The intermediate step generally obeys a logarithmic law for photographic paper. At very low intensities there seems to

be a limiting point of reaction. Also, in some cases there is a storage of energy so as to obtain effects similar to latent images. (Ref. 8, 22.)

(2) *Atmosphere:* (Ref. 1, 12, 15, 16, 39, 41.) By working in a vacuum, many fugitive dyes resist sunlight. There are a few rare exceptions. Gebhard says that under every-day conditions oxidation is the chief factor. The protective action of varnishes is, according to Toch, to prevent oxidation. Moisture in the air is favorable to the immediate action of light. Vapors of ammonia or alcohol greatly increase the action of light. Highly diluted acids, as found near towns, act protectively.

(3) *Dyes:* The constitution of the dyes has been studied in relation to fading by Gebhard and many others. Many of the coal-tar dyes are reported as fast as the best mineral pigments.

(4) *Fiber:* Many dyes have similar effects on silks and wools. With cottons, there are greater differences. On paper, it is very difficult to get a fast dye. (Ref. 35, 42.)

(5) *Mode of Applying Dye, Including Mordants, Filters, etc.*, and, in paints, nature of oil and varnish medium. The references cover details too complex to give here. (Ref. 9, 31, 36, 39, 44, 45, 52.)

(6) *Temperature:* In general, the temperature co-efficients of light reactions are small. I have, however, discovered exceptional results with lithophone, but even here the results are probably due to the superposition of secondary chemical actions. (Ref. 28, 29, 57, 67.)

C. Testing in Sunlight.

Tests have shown that the chemical action of sunlight often varies to double in power, although the sky may be clear. The sunlight varies because of variations in solar emission, shifting position of sun, and changing atmospheric conditions. Noon sunlight is usually several times stronger in action than four hours sooner or later. In the winter time the actinic values are several times lower than in the summer, and the day is only about half as long. Daylight means an expensive arrangement for protecting against rain, wind, etc. "One observer may expose his patterns in the open to the joint action of sunlight, wind,

rain, and possibly frost; another may expose under glass and place the patterns so as to get the largest possible proportion of the direct rays of the sun, or he may perhaps expose in diffused daylight only.

"Again, the depth of the shade, the climate, the condition of the atmosphere, the time of the year, are all important factors which must necessarily be taken into account if anything like an accurate result is to be arrived at. With the possibility of such varying conditions, it will be easily understood how one observer may obtain a result which leads him to infer that a color is not fast, whereas another, who may have exposed the same color for the same length of time, concludes that the color is fast. It is to be regretted that we have no recognized standard for testing of color as to their fastness to light, and much credit would be due to anyone who would take the trouble to work this out. It would undoubtedly be a step in the right direction if, when exposing to direct sunlight under glass, we could agree as to which position the board, on which the patterns are fixed, should be placed in, and in giving the result, mention the number of hours of direct sunlight (measured by the sun recorder) and of diffused light to which the patterns have been exposed. By a series of experiments, the ratio of destructive action of direct sunlight and the average of diffused daylight could possibly be determined, and we should thus be enabled to express the duration of exposure in one term, *viz.*, hours of direct sunlight. If this were done, there would be much less divergency of opinion regarding the fastness of colors to light. For exact measure, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates." (See Knecht, Rawson and Loewenthal, page 744.) The method of testing used by these gentlemen was to expose under glass, facing south, with part of the pattern covered with thick cardboard. "If it has stood a month's exposure in summer without any material alteration, it may be called fast."

My sunlight tests were made in June, without glass, under direct sunlight, and between 7.30 A. M. and 4.45 P. M. The patterns were placed horizontally. The patterns were taken indoors whenever the sun was obscured by clouds. Fifty hours

of such direct sunlight required between two and three weeks. The exposure was on the roof of a building receiving light from nearly all the sky as well as from the sun. I find that the actinic power of the blue sky varies between 20 and 50 percent of the total effect. By measuring the actinic effect of a ray of sunbeam let into a dark room, the light of the sky is largely eliminated. If the sky is overcast with clouds then the diffused light may become nearly 100 percent of the total.

In the literature (Ref. 5, 30, 32, 44, 51) summarized at the end of this article, it will be found that considerable work has been done to measure the changing actinic effect of sunlight, but a complete solution has not been secured. Gebhard (Ref. 33) points out that sunlight is variable in color as well as amount. The devices proposed for measuring chemical action of sunlight are clumsy, but it must be admitted are better than no effort at standardization. Probably the standardized results afford a variation of 20 percent. The unstandardized results are often such that the stronger effect may be twice the weaker.

Fig. 1.

D. The 5,000 M. S. C. P. White-Flame Arc.

The high amperage white-flame arc has been in use only a few years, but practically all photo-engravers have adopted it because of its efficiency, power and quality of light, which is the best known for color-process work. In Fig. 1 is shown in the center the spectrum of a carbon arc, in the region showing some of the strong cyanogen bands. These were photographed with a No. 2 2.5-inch (6 cm.) concave grating spectroscope.

The outside spectrum is that of the white-flame arc, which is seen to have an enormous number of light-giving lines filling the spaces between the cyanogen bands and superposed upon them, resulting in a better light than the enclosed arc even at the same or greater efficiency. The spectrum of the white-flame arc is *equally* rich in the green, yellow and red regions. The extreme closeness of the lines gives a light nearly the same in continuity

as sunlight, which also has its dark lines (Fraunhofer lines). The candle power of the high amperage white-flame arc is exceptional in tremendous size of unit available and of greater efficiency than other forms of illumination. The following table contains average results as to mean spherical candle power and mean spherical photographic power. The average relative time to affect equally solio paper with the lights in a two-meter sphere is the basis of photographic power. We can all admit, as Mees says, that this is no scientific definition. A 28-ampere Aristo lamp was used with white flame carbons under open arc conditions and without any globe. A comparison with the nitrogen-filled lamps is given:

TABLE I.

	Line Volts	Arc Volts	Amperes	Mean Spherical Candle Power	Mean Spherical Photo. Power
White-Flame Arc (open)	115	63	28.	5130	100
Nitrogen lamp—clear globe	117	117	6.7	866	4
Nitrogen lamp—blue globe.....	115	115	8.5	485	5

It is extremely conservative to say that for an equal amount of electrical energy the photographic power of the white-flame arc is six to ten times greater than that of the nitrogen filled incandescent lamp.

E. General Notes on Lamps Available.

The above tests were made with the Aristo lamp on direct current. Tests with alternating current show greater value, due to the response of the flame arc to the voltage component of the power and to other factors. The photographic power of the flame arc increases nearly four times when the current is doubled and is nearly proportional to the arc voltage. On a fluctuating line voltage it varies less than half as much as the nitrogen-filled incandescent lamp and is perfectly indifferent to all kinds of electrical and mechanical shocks. There is thus a greater service power for reproducing results. In most of these tests an Aristo lamp was used on 110 volts with the globe removed. An ordinary 5 ampere, enclosed arc lamp can be arranged with a shunt to carry 20 amperes at 55 volts around the lamp resistance and solenoid, to operate at 55 amperes at the flame arc. A publication of this arrangement will be made in detail later.

There are a large number of standard lamps on the market that can be adopted. The Macbeth, Bogue and Helios are commercial lamps used in photo-engraving. In some of the fading tests, a 220 volt Macbeth flame arc at 25 amperes and 90 arc volts was used.

F. Light of Different Flame Carbons.

The most valuable flame carbon for fading tests is the snow-white flame carbon. This has the maximum actinic power with or without the interposition of glass. Also it approaches very closely to sunlight with blue skylight. The flame carbons were used chiefly in 10 mm. x 305 mm. as lower positives with an ordinary ½ x 12-inch (1.3 x 30 cm.) enclosed arc cored upper carbon. In some cases ½ x 12-inch (1.3 x 30 cm.) flame cored carbons were used. The chief characteristics of these carbons are given in the following table:

Table II.

	Light	Photo. Power
Snow-white flame carbon	Like sunlight plus blue skylight	100
"Blue" flame carbon	Rich in ultraviolet	60
Yellow flame carbon	Rich in red, yellow and green	35
Red flame carbon	Rich in red	30
Pure carbon arc, (10 mm. shell)	Next to snow-white in quality	40

The photographic power represents the inverse of average time to attain equal shades with solio paper. The effect here is chiefly that of the short waves.

G. Test Arrangements.

The best arrangement so far has been with a set of 20-inch (50 cm.) hoops around the Aristo lamp at 28 amperes. This provided a good circulation of air to keep the samples cool and for carrying the arc products up. There were tested at the same time a couple of hundred of small samples secured from standard dye houses. Only a small piece of sample was exposed and the rest covered with heavy blotting paper. Then the other end of these same samples were exposed to sunlight for fifty actual hours of

sunshine. Also tests were made in front of a 25 ampere, 220 volt Macbeth lamp with 90 arc volts. In this case, a flat board was used and no correction for the change in distance from the light was possible. No doubt, much better arrangements can be developed.

H. Comparison of Action of Sunlight and White-Flame Arc.

A sample book entitled, "The 1912, Fashionable Colors," was obtained from Farbwerke vorm. Meister Lucius and Brüning, Hoechst am Main. This gave the following results for the standard color on wool. (The goods are dyed 1½ hours at the boil in an acid bath with addition of 10 to 20 lb. Glauber's salt and 3 to 5 lb. sulphuric acid or with 7½ to 12½ lb. tartar substitute. The amounts refer to 100 pounds of material.)

Percent	Dye	Standard Colors Exposed to 50 Hours June Sunlight
2	Flavazine L	No change.
2	Flavazine S	No change.
2	Flavazine T	No change.
2	Victoria Scarlet 2R	No change.
3	Brilliant Crimson O	No change.
2	Sulpho Rosazeine B	Darkens with loss of brightness.
1½	Amido Naphthol Red BB	No change.
1½	Amido Naphthol Red 6B	No change.
3	Alizarine Direct Blue E3BO	Darkens with loss of brightness.
1½	Patent Pure Blue O	Darkens with loss of brightness.
2	Patent Blue V new	Darkens with loss of brightness.
3	Naphthalene Green V	Darkens with loss of brightness.
2	Acid Violet 6BN	Slight change.
3	Amido Blue GGR	No change.

Viewing at an angle, the fading is of course lighter. The five dyes showing most effect alone are equally conspicuous in the mixtures. As the dye is diluted with unlike color, the effect becomes sharper. The effects in sunlight for 50 hours were duplicated by the light of the white flame in 10 to 20 hours. This was also true of the 132 mixtures. The fading action was far more marked with dilute solution. For example $\frac{1}{16}$ percent Sulpho Rosazeine B was nearly bleached, although 2 percent showed only a slight darkened effect viewed directly from above.

The action of light on Sulpho Rosazeine B was marked in mixtures, 25, 26, 27, 67, 68, 69, 73, 74, 75. These numbers refer to the 1912 book. The Patent Blue V new showed marked change in 10, 11, 12, 13, 14, 15, 127, 128, 129. The Patent Pure Blue O changed much in 67, 68, 69. The Alizarine Direct Blue showed marked changes in 4, 5, 6, 7, 8, 9, 13, 14, 15, 34, 35, 36, 49, 50, 51, 52, 53, 54. Dyes with Naphthalene Green V showed only slight changes. The most marked color change was with 127, 128 and 129. Here a bright blue changed to a reddish purple. No. 127 consisted of 0.6 percent Sulpho Rosazeine B, 0.15 percent Patent Blue V new, 0.02 percent Alizarine Direct Blue. All these colors separately are affected by light and hence the unusual effect on the composite is not surprising.

The 1914 Color Book of the Farbwerke vorm. Meister Lucius & Brüning, Hoechst am Main, shows a marked improvement in the fastness to light of the dyes of the 1912 book. None of the color mixtures faded nearly as much as those of 1912. In these tests 50 hours of sunlight was compared with 25 hours of the light of a 220 V. 25 A. Macbeth white-flame arc at two feet distance. The flame arc light had the same kind of an effect as sunlight. With the blues and greens, there was fading as before, and no change occurred with 2 percent yellows or reds. The troublesome Sulpho Rosazeine B (of 1912) was eliminated. A new brown (Amido Yellow E, pat.) had been added. This darkened a little.

The Amido Naphthol Red BB at 0.6 percent showed a little fading. A mixture (No. 125) of 0.6 percent Amido Yellow E, 0.06 percent Alizarine Direct Cyanine 3 G and 0.009 percent Patent Blue V new, showed a change from olive green to a decided brown. The Naphthol Green V and Patent Blue V new showed the most change under light.

Cassella Color Company—Catalogue No. 3317, Dyestuffs for Wool, gave the following results, comparing 50 hours sunlight and 20 hours light of white-flame arc at 10 inches (25 cm.), with good ventilation. The white flame arc gave nearly the same effect as sunlight, for this reason a separate column is not given except for 100 hours with the flame arc, equivalent to about a year of ordinary light.

	50 HOURS SUNLIGHT		100 HOURS FLAME ARC	
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Fast Acid Yellow 3G	No change	No change	Slightly darker	Slightly darker
Fast Acid Yellow TL	" "	" "	" "	" "
Naphthol Yellow S	Faded	Darkened	Much faded	Much darker
Acid Yellow AT	No change	No change	No change	No change
Milling Yellow G pat	" "	" "	" "	" "
Milling Yellow O pat	" "	" "	Faded	Darker
Fast Yellow S	" "	" "	"	"
Metanil Yellow	Slight	Slight	"	"
Indian Yellow FF	Darkened	Darkened	Much darker	Much darker
Indian Yellow R	"	"	" "	" "
Indian Yellow G	Much darkened	Much darkened	" "	" "
Tropaeoline G	Slightly faded	Darkened	Faded	" "
Tropaeoline OO	" "	"	"	" "
Orange IV	" "	"	"	" "
Orange GG	No change	No change	Slightly faded	No change
Orange EN	" "	" "	" "	" "
Orange II	" "	" "	No change	" "
	1 PERCENT	2 PERCENT	1 PERCENT	2 PERCENT
Orange Extra	No change	No change	Slightly faded	No change
Orange R	" "	" "	" "	" "
Orange ENZ	" "	" "	" "	" "
	2 PERCENT	4 PERCENT	2 PERCENT	4 PERCENT
Scarlet FR	No change	No change	Slightly faded	No change
Scarlet FRR	" "	" "	" "	" "
Scarlet FRRR	" "	" "	" "	" "
Brilliant Scarlet GG	" "	" "	" "	" "
Brilliant Scarlet G	" "	" "	" "	" "
Brilliant Scarlet R	" "	" "	Faded	" "
Brilliant Scarlet RR	" "	" "	"	Slightly faded
Brilliant Scarlet 3R	" "	" "	"	" "
Brilliant Scarlet 4R	" "	" "	"	Faded
Brilliant Scarlet 6R	" "	" "	"	"
Crystal Scarlet 6R	" "	" "	Slightly faded	No change
Brilliant Cochineal 2R	" "	" "	" "	" "
Brilliant Cochineal 4R	" "	" "	" "	" "
Brilliant Croceine B	" "	" "	" "	" "
Brilliant Croceine M	" "	" "	Faded	" "
	2 PERCENT	4 PERCENT	2 PERCENT	4 PERCENT
Brilliant Croceine MOO	No change	No change	Faded	No change
Brilliant Croceine 3B	" "	"	"	" "
Brilliant Croceine 5B	" "	"	"	" "
Brilliant Croceine 9B	" "	"	"	" "
Croceine AZ	" "	"	"	" "
Azo Rubine	Slight fading	Very slight	"	" "
Roccelline	" "	" "	"	" "
Naphthol Red EB	" "	" "	"	" "
Naphthol Red C	" "	" "	"	Slightly faded
Amaranth	" "	" "	"	No change
Azo Red A	" "	" "	Much faded	Faded
Amaranth B	No change	No change	Slightly faded	No change
Wool Red B	" "	" "	" "	" "
Milling Red FR	" "	" "	" "	" "
Milling Red G	" "	" "	" "	" "
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Lanafuchsine SG	Slight fading	Very slight	Faded	Slightly faded
Lanafuchsine SB	" "	" "	"	Faded
Lanafuchsine BBS	" "	" "	Much faded	"
Brilliant Lanafuchsine GG	" "	" "	" "	No change
Brilliant Lanafuchsine SL	" "	" "	" "	" "
Brilliant Lanafuchsine BB	" "	" "	" "	" "
Azo Orseille BB	" "	" "	" "	" "
Lanafuchsine 6B	" "	" "	" "	" "
Acid Magenta	" "	" "	" "	Darker
Archil Substitute N powder	Faded	Slight fading	" "	Slightly faded
Acid Violet 4RS	"	" "	" "	Faded
Azo Wool Violet 7R	Slight fading	Very slight	" "	Slightly faded
Alkaline Violet CA	Faded	Darkened	" "	Faded
Formyl Violet 4BF	"	"	" "	"
Formyl Violet S4B	"	"	" "	"
Formyl Violet S5B	"	"	" "	"

	50 HOURS SUNLIGHT		100 HOURS FLAME ARC	
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Formyl Violet 6B	Faded	Darkened	Much faded	Faded
Formyl Violet 10B	"	"	" "	"
Acid Violet 6BS	"	"	" "	"
Acid Violet 6BC	"	"	" "	"
	3 PERCENT	5 PERCENT	3 PERCENT	5 PERCENT
Azo Fast Violet 2R	No change	No change	Slightly faded	No change
Azo Wool Violet 4B	" "	" "	Faded	Slightly faded
Azo Fast Blue B pat	Slight	" "	"	" "
Azo Fast Blue BD pat	No change	" "	"	" "
Azo Fast Blue BR conc. pat.	" "	" "	"	" "
Azo Wool Blue 6B pat	Slight	" "	Much faded	Faded
Azo Wool Blue SE pat	"	" "	" "	"
Azo Wool Blue B pat	"	" "	" "	"
Azo Wool Blue SER pat	"	" "	" "	"
Azo Wool Blue C pat	No change	" "	" " *	" *
Azo Navy Blue 3B pat	Slight	" "	Faded	"
Azo Navy Blue B pat	"	" "	"	"
Brill't Naphthol Blue 4B pat	"	" "	"	"
Brill't Naphthol Blue B pat.	"	" "	"	"
Brill't Naphthol Blue R pat.	"	" "	"	"
Acid Navy Blue A pat	"	" "	"	"
Fast Navy Blue G pat	No change	" "	Slightly faded	Slightly faded
Fast Navy Blue B pat	" "	" "	" "	" "
Azo Merino Blue G pat	" "	" "	" "	" "

* Redish tint at end.

	3 PERCENT	5 PERCENT	3 PERCENT	5 PERCENT
Azo Merino Blue 3B pat	No change	No change	Slightly faded	Slightly faded
Peri Wool Blue G pat	" "	" "	No change	No change
Peri Wool Blue B pat	" "	" "	" "	" "
Lanacyl Blue BB pat	" "	" "	" "	" "
Lanacyl Blue BN	" "	" "	" "	" "
Lanacyl Blue R pat	" "	" "	" "	" "
Lanacyl Blue RN	" "	" "	" "	" "
Lanacyl Navy Blue BB pat	" "	" "	" "	" "
Lanacyl Navy Blue B pat	" "	" "	" "	" "
Lanacyl Violet BF pat	" "	" "	" "	" "
Naphthol Blue G	" "	" "	" "	" "

	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Cyanole FF	Faded	Darkened	Much faded	Faded
Cyanole extra	"	"	" "	"
Cyanole extra H	"	"	" "	"
Cyanole AB	"	"	" "	"
Tetra Cyanole extra	"	"	" "	"
Tetra Cyanole SF	"	"	" "	"
Tetra Cyanole V	"	"	" "	"
Tetra Cyanole A	"	"	" "	"
Thiocarmine R powder	"	"	" "	"
Cyanole Navy Blue KR	"	"	" "	"
Indigo Blue N	Very faded	Faded	" "	"
Indigo Blue SGN	" "	"	" "	"
Formyl Blue B	" "	Darkened	" "	"
Brilliant Milling Blue B	" "	"	" "	"
Alizarine Cyanole EF pat	Faded	No change	" "	"
Alizarine Cyanole SR pat	"	" "	" "	"
Alizarine Cyanole SB pat	"	" "	" "	"
Alizarine Cyanole SG pat	"	Slight change	" "	"
Alizarine Cyanole Violet R pat	"	No change	Faded	Darker
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Alkaline Blue 6B	Faded	Slight fading	Much faded	Faded
Alkaline Blue 4B	"	" "	" "	"
Alkaline Blue 3B	"	" "	" "	"
	0.9 PERCENT	2.3 PERCENT	0.9 PERCENT	2.3 PERCENT
Alkaline Blue 2R	Faded	Slight fading	Much faded	Faded
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Pure Soluble Blue	Faded	Very slight	Much faded	Faded
Water Blue B	"	Darkened	" "	"
Water Blue RB	"	No change	" "	"
Water Blue R	"	" "	" "	"

	50 HOURS SUNLIGHT		100 HOURS FLAME ARC	
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Blue RS	Faded	No change	Much faded	Faded
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Wool Blue TB	Faded	No change	Much faded	Faded
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Acid Green 5C	Faded	Faded	Much faded	Faded
Acid Green extra conc.	"	Darkened	" "	"
Acid Green extra conc. B	"	"	" "	"
Cyanole Fast Green G pat.	"	"	" "	Darker
Brilliant Milling Green B	"	"	" "	Faded
Fast Acid Green BN	"	"	" "	"
Cyanole Green 6G	"	"	" "	Darker
Cyanole Green S	"	"	" "	"
Cyanole Green B	Slightly faded	"	" "	"
Alizarine Brill't Green G pat.	No change	No change	Slightly faded	No change
	2 PERCENT	6 PERCENT	2 PERCENT	6 PERCENT
Naphthol Green B	No change	No change	Faded	Darkened
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Naphthol Dark Green G	Slight fading	No change	Much faded	Faded
	4 PERCENT	7 PERCENT	4 PERCENT	7 PERCENT
Naphthol Black 6B	No change	No change	No change	No change
Naphthol Black 3B	" "	" "	" "	" "
Naphthol Black SG	" "	" "	" "	" "
Naphthol Black B	" "	" "	" "	" "
Naphthol Black P	" "	" "	" "	" "
Naphthol Blue Black SB	" "	" "	" "	" "
	3 PERCENT	5 PERCENT	3 PERCENT	5 PERCENT
Naphthol Blue Black S	No change	No change	No change	No change
Naphthol Blue Black	" "	" "	" "	" "
Some thirty other blacks showed no change.				
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Silver Grey N	Faded	Faded	Much faded	Much faded
Nigrosine soluble in water	"	"	" "	" "
Aniline Grey B	"	"	" "	" "
Induline B	"	"	" "	" "
	2 PERCENT	4 PERCENT	2 PERCENT	4 PERCENT
Solid Blue R	Very slight	No change	Slightly faded	Darker
Solid Blue 3R	No change	" "	" "	No change
	3 PERCENT	5 PERCENT	3 PERCENT	5 PERCENT
Gloria Black B	No change	No change	No change	No change
Neutral Wool Black 4B	" "	" "	" "	" "
Neutral Wool Black B	" "	" "	" "	" "
Azo Wool Black G	" "	" "	" "	" "
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Eosine 3G	Faded	Darkened	Much faded	Much faded
Eosine GGF	"	"	" "	" "
Eosine BN	"	"	" "	" "
Erythrosine B	"	Faded	" "	" "
Erythrosine extra N	"	"	" "	" "
	1 PERCENT	3 PERCENT	1 PERCENT	3 PERCENT
Phloxine S	Faded	Darkened	Much faded	Much faded
	0.5 PERCENT	1.5 PERCENT	0.5 PERCENT	1.5 PERCENT
Phloxine	Faded	Darkened	Much faded	Much faded
Rose Bengale extra N	"	"	" "	" "
Rosazeine B	Slightly faded	No change	Faded	Faded
	0.1 PERCENT	0.3 PERCENT	0.1 PERCENT	0.3 PERCENT
Rozazeine B extra	Very slight	No change	Faded	Faded

A series of ninety chromated dyes showed no change in 50 hours of sunlight or in the light of white flame arc for 20 hours.

A series of sixty diamine dyes showed a few fading of blue in sunlight. The tests in the flame arc light were not completed, but the action was in same direction as far as tested.

Some aniline colors from The Heller and Merz Company gave the following results:

On Wool	50 Hours Sunlight	10-20 hrs. Flame Arc, 10 in. (25 cm.)
Patent Blue B	Darkened	Darkened
Acid Violet 4BNS	Darkened	Darkened
Acid Green 2GX	Darkened	Darkened
Naphthol Yellow L	Darkened	Darkened
Chrysophenine E. S. Conc.	Slight darkening	Slight darkening
Scarlet 4R Brilliant	No change	No change

These also resisted distilled water except the blue. The yellow and blue were most affected by light.

On Cotton	50 Hours Sunlight	10-20 hrs. Flame Arc, 10 in. (25 cm.)
Pheno Blue 7B Conc.	Darkened	Darkened
Pheno Violet BK Conc.	Slightly darkened	Slightly darkened
Pheno Green KDX	Slight change	Slight change
Primuline Conc.	Much darkened	Much darkened
Chrysophenine E. S. Conc.	Slight change	Slight change
Pheno Orange R	Darkened	Darkened
Pheno Fast Scarlet 4B	Darkened	Darkened

All these cotton dyes, except the light yellow gave colored solutions with distilled water. In 6 hours direct sunlight the yellow had darkened to a brownish yellow. The action of the white flame arc light was the same as sunlight. With cottons and the Macbeth 220 volt at two feet, some fading was obtained in two hours for Primuline conc., Pheno Violet 3K conc. and Chrysophenine E. S. conc.

Some cheap bunting (retailing at 5 cents a yard) was secured from a store in Cleveland. These were said by the merchant not to be fast to light.

Color	50 Hours Sunlight	8½ hrs. Macbeth Lamp, 2 ft. (60 cm.)
Black	No change	No change
Violet	Greatly faded	Faded
Dark Blue	Greatly faded	Slight fading
Baby Blue	Change to pure white	Bleached
Dark Green	Faded	No change
Light Green	Change to pure white	Nearly bleached
Yellow	Greatly faded	Nearly bleached
Red	Turned brown	No change
Purple	Greatly faded	Nearly bleached

The four most rapidly fading buntings were made the basis of several comparisons as to effect of increasing increments by 1 hour of exposure, of effect of light from different flame carbons, of light from different flame lamps and of comparison of D. C. and A. C.

Tests on bunting, using an Aristo 28 ampere, 110 volt lamp with white flame carbons and using hoop of 20 inch (50 cm.) diameter. Exposures were in steps of one hour increments. The significant data are:

	1ST HOUR	2D HOUR	4TH HOUR	10TH HOUR
Baby Blue	Slightly faded	Faded	Bleached	Bleached
Pink	Faded	Much faded	Bleached	Bleached
Purple	Slightly faded	Faded	Nearly bleached	Bleached
Light Green	Very slight	Slight fading	Faded	Much faded

These now afford a basis for measuring time of fading to equal extent by other forms of illumination.

	CORRESPONDING TIME WITH ARISTO AT 10 INCHES (25 CM.)			
LIGHT USED	BABY BLUE	PINK	PURPLE	LIGHT GREEN
220 V., 25 A., White flame arc at 2 ft..	1 hour	1 hour	1 hour	1 hour
" " "Blue" flame arc.....	2 hours	3 hours	5 hours	2 hours
" " Yellow flame arc.....	1 hour	1 hour	1 hour	No change
" " Red flame arc.....	No change	No change	No change	No change
" " Pure carbon arc.....	2 hours	3 hours	5 hours	2 hours

The "Blue" flame arc was very rich in ultraviolet light and had over twice the effect on the purple as on the baby blue or light green. It is unfortunate from the standpoint of dye fading that ultraviolet light often has very different proportional results on different dyes as compared with sunlight. With only two hours' exposure, the other buntings except the yellow showed practically no change. The light green and purple were faded a little more with sunlight at 50 hours than the Aristo at 10 inches (25 cm.) for 10 hours. The brightest June sunlight and skylight for 50 hours was more effective than 10 hours with Aristo at 10 inches (25 cm.) and less effective than 20 hours. The Aristo at 10 inches (25 cm.) was twice as powerful as the 220 volt Macbeth at two feet (60 cm.).

Comparison with a nitrogen filled lamp on 110 volts D. C. at 6½ amp. 750 watt unit with clear glass.

Table showing time for equal effect Aristo at 10 inches (25 cm.) with nitrogen lamp at 10 inches (25 cm.) for one hundred hours:

	Time of Equal Effect Aristo	Times Greater Speed with Flame Arc
Baby Blue	3 hrs.	33
Pink	1 hr.	100
Purple	3 hrs.	33
Light Green	6 hours	17

The action of the incandescent light on the other bunting was as follows:

Black	No effect
Violet	Faded
Deep Blue	Faded
Green	Faded (more blue tone)
Yellow	Slightly faded
Red	No effect

The large excess of red and yellow rays and deficiency of blue rays has increased the action on the green (yellow absorbed) and decreased the action markedly on the red and yellow. The colors most easily faded by the incandescent lamp are the green and least easily faded are the reds and yellows.

Some comparisons were made between the D. C. Aristo and A. C. Aristo with a material advantage for the A. C. in speed.

Tests on linens. A little over one hundred samples of colored linens were exposed on separate parts to 50 hours sunlight and 10 hours white flame arc at 10 inches (25 cm.). The 10 hours of the white flame arc gave in all cases more effect than 50 hours of sunlight. This 50-hour period was not at the same time as the first set with the wools and cottons. The sky was somewhat murky and at times there were some small fleeting clouds during two of the days of the test. All the samples faded by sunlight were faded to a greater degree by the light of the white flame arc. Excepting black, none of the samples of dyed linen could resist 10 hours with the white flame arc.

I. Action of Paints, with Special Reference to Lithopone.

A number of sample books of the National Lead Company and Sherwin-Williams Paint Company were exposed to sunlight and to the light of the white flame arc and the similarity of action was noted. Samples supposed to contain chrome yellow turned green, perhaps by a reducing action of organic matter on the

chromate. In many cases the tints were brightened by the bleaching of the linseed oil, etc.

Some tests by Mr. B. Perris, of the National Carbon Company, showed considerable fading of the best enamel sign paints after one hundred hours exposure to light of a 25 ampere, white flame arc at 2 feet. This test is probably about equivalent to one year of ordinary sunshine in this latitude.

Lithopone ($ZnS.BaSO_4$) under the action of the light did not respond as rapidly as expected. Lithopone is well known to turn grey or even black on exposure to intense light, and later this dark color may turn to pure white in the absence of light or even in subdued light. Mr. O'Brien (ref. 55) has published an interesting article on the cause of the changes in color of lithopone. Two samples of lithopone were made up with a 1 percent solution of gum arabic and painted on glass with a camel's hair brush. This was allowed to dry and then it was exposed with the paint side to the light. The response was slight and mostly at the protected edges directly two feet (60 cm.) in front of the 220 volt Macbeth flame arc. I believed that the heat of the flame arc hastened the oxidation of the black zinc metal film as fast as formed and so I arranged the experiment with part of the plate cooled by being fastened by rubber bands on a large block (25 lb.-11 kg.) of ice. The part now kept cool by the ice blackened in a fraction of an hour and the part not cooled by the ice remained white after several hours. This experiment was conclusively repeated several times and proves the great importance of temperature as regards the blackening of lithopone under light. Under fifty hours of sunlight the lithopone darkened greatly. The interposition of glass, greatly decreased the effect.

The following table shows that the maximum darkening of lithopone is given by the light of the "blue flame" arc due to its large amount of ultraviolet light. The tests were made at two feet (60 cm.) with 25 amps. arc at 90 arc volts on 220-volt D. C. line. Samples ice cooled.

	Exposure of ½ Hour	On Standing in Dark
White flame	Blackened	White few hours
"Blue" flame	Rapidly blackened	Black after week
Yellow flame	Blackened	Black after week
Red flame	Blackened	White one hour

The parts not ice cooled remained white in all cases.

The blue flame arc gave the most effect. By exposing for five hours and keeping cool with ice, black coatings were obtained that were still black after one week. I have carefully read Mr. O'Brien's article and find no mention of this temperature effect, which appears to me to admirably support his theory of the cause of the blackening and subsequent whitening of lithopone. It also gives an added reason why lithopone is so well suited for interiors, with their higher temperatures.

J. Conclusions.

(1) For dye and paint testing as to fastness to light, there is found in the high amperage flame arc a light more powerful than sunlight, and, unlike sunlight, exactly reproducible.

(2) Different colored flame effects can be secured by using specially designed carbons which give colored lights as follows:

Snow-white flame carbons, nearly equal to sunlight plus blue sky.

"Blue" flame carbons, strong ultraviolet light.

Yellow flame carbons, rich in red, yellow and green but weak in blue. Some violet and ultraviolet.

Red flame carbons, strong in red light.

Pure carbon arc, far inferior to the snow-white flame arc.

(3) Hundreds of dyes have been compared in best June sunshine and in the light of the snow-white flame arc, with essentially similar results, but at much greater speed.

(4) The best June sunlight for 50 hours gave an effect equal to between 10 and 20 hours of 28 ampere white flame at 10 in. (25 cm.). A more definite statement is impossible owing to the large variations of sunlight on even clear days.

(5) The 750-watt nitrogen-filled incandescent lamp required 17 to 100 times greater exposure for equal effect at like distance than a 28-ampere flame arc with 55 volts at the arc. A deficiency in the blue in the light of the incandescent lamp caused considerably different results from sunlight.

(6) The "Blue Flame" arc was rich in ultraviolet light and therefore caused, with different dyes, results not proportional to sunlight.

(7) With the white flame arc tests could be made in 10 hours, requiring otherwise about two weeks with sunlight under the change of weather common in the northeastern part of the United States.

(8) Some cheap buntings (pink, baby blue, pale green) showed fading in one hour with the light of the white flame arc.

(9) Fading was most marked with diluted dyes. Same also shows in complex mixes.

(10) The 1914 colors showed marked improvements over the 1912 colors as regards fastness to light.

(11) Lithopone gave the maximum darkening (also of greatest persistency) by exposure to the light of the "blue flame carbons" rich in ultraviolet light.

(12) Experiments on lithopone showed maximum action at low temperatures. This result supports the theories of O'Brien and Bancroft on the cause of the darkening of lithopone. Also it gives an added reason why lithopone is especially suited for interior painting.

In conclusion, I hope that this work will prove a basis for many new investigations of both the practical and scientific aspects of the chemical action of light on dyes and paints. I here take pleasure in thanking those who have aided in this work. Dr. W. C. Moore, I thank for friendly aid; Mr. P. P. Bethea for care in experimentally following my directions, and I am under obligation to The National Carbon Co., whose facilities I enjoyed in doing this work. Also, in the matter of samples, I have occasion to thank the firms Meister Lucius and Brüning, Heller and Merz, Cassella Color Co., Mott & Co., Sherwin-Williams Paint Co., and others.

K. Brief Summary of Literature.

The following are a few of the more important references. As this subject is as old as civilization, a complete bibliography would be out of question.

1. Jules Joffre: Bulletin de la Societé Chimique de Paris [3], **I**, May 5, 1889.

Chevreul (1837) showed that most dyes were not discharged in vacuum, but tumeric and prussian blue formed exceptions.

Joffre found that most shades were unaffected in pure nitrogen, but those with picric acid were exceptions. The action of oxygen of air can also be eliminated by paraffin.

2. Depierre and Clouet: Jour. Soc. Dyers and Col., 1885, p. 245.

Seventy-six typical coloring matters on calico were examined in different colored light.

Strongest Action	Least Action	On Material Dyed
Yellow rays	Red rays	Red
Blue rays	Red rays	Orange, Yellow, Green
Yellow rays	Red rays	Blue
Blue rays	Red rays	Violet

3. Decoux: Jour. Soc. Dyers and Col. (1885), p. 247.

Electric arc light resembles sunlight in its action, but at 1.5 meters had one-fourth the effect of sunlight.

4. Dufton: Jour. Soc. Dyers and Col. (1885), p. 245.

Colors of light complementary to the dyed fabric act most rapidly. The dyed color is not appreciably affected by a light of the same color.

5. Dosne: Jour. Soc. Dyers and Col. (1901), p. 42.

Need of measuring the changing intensity of sunlight.

6. Brownlie: Jour. Soc. Dyers and Col. (1902), p. 295.

Ammonia, alcohol, or pyridine vapors enormously increase the action of light on dyes. Naphtha and chloroform slightly retard it.

7. Brit. Assoc. Reports, Section B, 1893, 1894, 1895, 1896 and 1898. See Chemical News, **64**, 119; **68**, 155, 170; **70**, 154; 169, **74**, 205, 218; **78**, 175; 205, 215.

Several hundred commercial dyes of all colors at 2 percent on various fibres were tested under glass against sunlight and daylight in sets, for 5, 10, 15, 35, and 55 weeks. Colors were divided in five classes as to fastness.

8. Weigert: Ann. Physik (1908), **24**, 243-66.

Chemical action under light. "Active" condition after removal of light. Temperature coefficients of light reactions in general are small.

9. Hoffman: Text. Färber Ztg. (1907), **6**, 779.

Examination of colors in artificial light.

10. Toch: J. Soc. Chem. Ind. (1908), **37**, 311.

Influence of sunlight on paints and varnishes. Glass is protective, red slightly more than blue. Theory of carbon separation in bitumen paints under light. Lithopone changed. Varnish keeps out oxygen. Linseed oil bleaches, due to action of light on green chlorophyll.

11. Gebhard: Zeit. fr. Farb. Industrie (1909), **7**, 299.

Cause of action of light on colors.

12. Bolis: Rev. gen. mat. color. (1909), **12**, 289.

Fastness of dyes to light. Decreased by moist air. Less with blue than with red rays. Vacuum little or no action.

13. Huble: Wiener Mitth. (1909), **14**, 268.

Glycerol increases light sensitiveness of some dyes five hundred fold.

14. Immerheiser: Text. Farb. Ztg. (1910), **7**, 457.

Fastness of coal tar colors.

15. Gebhard: J. Soc. Dyers' Colorists (1910), **26**, 173; (1910), **25**, 276, 304; Z. angew. Chem. (1910), **22**, 2484.

Bleaching of dyes by light depends on (a) oxidation, and (b) formation of peroxide hydrates.

16. Weigert: Ber. (1910), **43**, 164.

Some dyes in oxygen-free nitrogen under light show pressure and color changes.

17. Gebhard: Ber. (1910), **43**, 751.

Defends oxidation theory against Vogel and Weigert.

18. Gebhard: Z. angew. Chem. (1910), **22**, 1890.

Broadens oxidation theory. Shows that O-H and S-H groups decrease fastness and NO_3 group increases fastness.

19. Gebhard: Färber-Ztg. (1910), **21**, 95.

Disputes Witt's hypothesis of dyestuffs absorbing and transforming long to short waves capable of producing chemical change.

20. Krais: Z. angew. Chem. (1911), **24**, 481.

Modern light-fast wall paper guaranteed for five years. Colored by protected metal powders.

21. Krais: Chem. Ztg. (1911), **35**, 146.

Fastness of coal tar dyes in paints.

22. Gebhard: Chem. Ztg. (1911), **35**, 273, 290.

Light in relation to chemical action. Influence of wave-length, intensity, catalyzers, and photo chemical after-effect.

23. Gebhard: Färber-Ztg. (1911), **22**, 6, 26.

The present method of testing fastness of colors with daylight is unsatisfactory, due to varying atmospheric conditions. Gebhard proposes using a cabinet with both enclosed arc and mercury quartz arc. The change of color whether fading or change to other tint is to be recorded by orthochromatic photography with a light-filter of same color as original dyeings.

24. Scheurer: Bull. soc. ind. Mulhouse (1911), **80**, 324.

The mercury quartz arc, with dyes protected against ozone, gave results different from sunlight. Benzo colors were hardly faded by sunlight, but in 24 hours by the Hg. quartz arc. Indigo resisted Hg. quartz arc light better than sunlight.

25. Valenta: Photo. Rundschau (1911), **25**, 56.

Sensitizing action of thiosinamine, etc.

26. Gebhard: Färber-Ztg. (1911), **21**, 253, 1910.

The oxidation theory of fading is experimentally confirmed. Permanency of dyeing affects permanency of the fiber. $CuSO_4$ improved the lightfastness of dithioalkyl-thioindigo and prevented at the same time the weakening of the fiber.

27. Kummell: Z. wiss. Phot. (1911), **9**, 54.

Bleaching is the result of oxidation. H_2O_2 and many sensitizers are studied.

28. Bacon: Philipp. J. Sci. (1911), **5**, 281.

The reaction of oxalic acid and uranium salts under light is investigated as to factors significant in dye fading. H_2O_2 factor, concentration Ur., temperature coefficient, etc., are reported on.

29. Schwezow: Z. wiss. Phot. (1911), **9**, 65.

Small temperature coefficients of bleaching of dyes.

30. Dosne: Rev. gen. Mat. color. (1911), **14**, 193.

An attempt to measure the changing intensity effect of sunlight.

31. Neuberg: Biochem. Z. (1911), **29**, 279.

Iron salts act like those of uranium on organic compounds under light.

32. Krais: Z. angew. Chem. (1911), **24**, 1302.

A test paper is arranged to measure the varying chemical action of the sunlight. Sun hours were shown to vary 100 per-cent from "bleach hours."

33. Gebhard: Z. angew. Chem. (1911), **24**, 1807, 2426.

Criticism of Krais' proposal. Sunlight varies in color and composition, and system is clumsy. A list of dyes, decomposed chiefly by red and yellow light, is given. Also a list for short waves and for long and short waves.

34. Klemperer: Färber-Ztg. (1911), **22**, 209.

The three primary colors are measured as to change by Kallab app. and plotted against time.

35. Maddox: World's Paper Trade Rev. (1911), **56**, 392.

Sunlight greatly deteriorates colored papers.

36. Eibner: Chem. Ztg. (1911), **35**, 753, 786.

Tests of paints. Acceleration of effects with certain zinc compounds.

37. Gebhard: Phot. Korr. (1912), **58**, 634.

Methylene blue with glycerol or HCHO bleaches in reduction by sunlight more rapidly in vacuo.

38. Gebhard: J. prakt. Chem. (1912), **84**, 561.

Relation between the sensitiveness to light and the constitution of dyes.

39. Bancroft: Orig. Com. 8th Intern. Congr. Appl. Chem. (1912), **20**, 59.

Permanency of painting. The color change of pigments caused by light is usually an oxidation. A drier in the oil may cause

reduction of the pigment. Rapid tests for fastness to light may be made with solution of peroxides and persulphates.

40. Bancroft, Elsenhost, Grant: Orig. Com. 8th Intern. Congr. Appl. Chem. (1912), **20**, 91.

Rapid testing of bleaching action of peroxides, etc., is suggested as a qualitative test of the stability of dyes.

41. Gebhard: Z. angew. Chem. (1912), **23**, 820.

The formation of peroxides under action of light on dyes is shown by chemical tests. The limited action in dry air is apparent, since the peroxides thus formed bleach just as rapidly as soon as moisture is introduced.

42. Krais: Z. angew. Chem. (1912), **23**, 1206.

Coal-tar dyes on carpets, embroidery cotton, resist light better than natural plant dyes. No light-resisting dyes have been found for paper or wood.

43. Valenta: Chem. Ztg. (1912), **33**, 1165.

Fastness to light and behavior of different coal-tar dyes taken as printing colors.

44. Krais: Z. angew. Chem. (1913), **25**, 2193.

Out of 63 coal-tar dyes, 40 were good as to light fastness and 11 were as satisfactory as the best mineral colors. Some dyes were found to be fast when exposed alone, but were faded when mixed with "blanc fixe." Tests of water colors behind glass, using "bleaching hours" method.

45. Krais: Z. angew. Chem. (1913), **26**, 74.

Tests in oil of light fastness of coal-tar dyes. No difference between behind glass and in open, for oil colors. Some 20 coal-tar dyes were as stable as the best mineral pigments.

46. Eibner and Gerstacker: Chem. Ztg. (1913), **37**, 137, 178, 195.

Action of light on Turnbull's blue, etc.

47. Harrison: J. Soc. Dyers' Colorists (1913), **28**, 225.

Besides oxidation, reduction theory is also used for several types of change under the action of light.

48. Gebhard: Chem. Ztg. (1913), **37**, 601, 622, 638, 662, 679.

Criticizes Harrison's results and defends oxidation theory.

Under the conditions of daily life, the fading of dyeings is due to oxidation process. The reducing properties of fibers are, contrary to Harrison, without influence upon the light-fastness of dyeings.

49. Gebhard: Z. angew. Chem. (1913), **26**, 79.

Oxidation in the light may be wholly different from that in the dark, even when the same oxidizing agent is used. Light of different wave lengths may cause the oxidation to proceed in different ways. Hence the limitations of the chemical method proposed by Dr. Bancroft.

50. König: Färber Ztg. (1914), **24**, 366.

Influencing the light fastness of dyeings.

51. Official report of committee on fastness of dyes of the section for dyes and textile industries of the Society of German Chemists. Z. angew. Chem. (1914), **27**, 57.

52. Tauber: Farben Ztg. (1914), **19**, 475.

Methods of testing the injurious effect of zinc whites on the stability of water colors, on exposure to light.

53. Ragg: Farben Ztg. (1913), **18**, 578.

The behavior of white zinc, white lead, and lithophone in paint colors.

54. Engelmann: Ger. Pat. 264,904 of 1912.

Manufacture of lithopone stable to light.

55. W. J. O'Brien: Jour. of Phys. Chem. (1915), **19**, 113.

A study of lithopone. The light of a 25A Macbeth printing lamp with flame carbons was found more satisfactory for most purposes than sunshine.

56. Bancroft: Jour. of Phys. Chem. (1915), **19**, 145.

The fastness of dyes to light, water, etc., is discussed. "The whole question of fastness to light is in a very bad way, because so little systematic work has been done. About all that I can hope to do at present is to point out how much we do not know in the hope that some enthusiastic person will fill in some of the gaps in our knowledge some day." Discussion is given of a number of protective factors and references to literature.

57. British Commercial Gas Association: Abstracted, American Gas Light Journal (22 Feb., 1915), **102**, 116.

The influence of temperatures, products, and light of gas illumination is found to be very small, compared to a little daylight.

58. Crookes: Dyeing and Calico Printing. Published 1874, Longmans, Green & Co., pages 655 to 661.

A valuable discussion is given of the influence of light on all kinds of colors. Madder should be ground in the dark. "Mordants also, especially the preparations of iron and tin, lose their affinity for the fiber, and are rendered worthless by even a short exposure to direct sunlight." Out of 60 typical dyes, only three resisted the sunshine of three summer months. Over two-thirds were changed in less than 8 days.

59. Laycock, Rawson, Gardner: A Dictionary of Dyes, Mordants, etc. Published 1901, J. B. Lippincott Co., page 139.

Summary of Brit. Assoc. Report over five years' experiments of action of light on dyes.

60. Barrows: Electrical Illuminating Engineering. Published 1908, McGraw Publishing Co., page 150.

Comparison of ultraviolet light of mercury arc and several months of tropical sunlight.

61. Zerr, Rubencamp, Mayer: "A Treatise on Color Manufacture." Published 1908, J. B. Lippincott Co., page 71.

"Exposure to the direct sunlight is a drastic test, under which fugitive colors will show a remarkable change in the course of a day."

62. Zerr and Mayer: "Tests for Coal-Tar Colors in Aniline Lakes." Published 1910, J. B. Lippincott Co., page 227.

The fastness to light of coal-tar color lakes.

63. Fay: "Coal-Tar Dyes." Published 1911, D. Van Nostrand Co., Indigo—5,000 years old, page 375.

64. Knecht, Rawson, and Loewenthal: A Manual of Dyeing. Published 1910, J. B. Lippincott Co., pages 743 to 748.

There is an excellent discussion, with references, in this book. The diversity of testing methods is brought out. Some test by exposure to weather, some under glass, some to diffused sky-

light, and some to combined skylight and sunlight. Some test in a horizontal position and some in a vertical. "For exact measurements, however, it would be necessary to measure the average intensity of the sun's rays during the different seasons of the year and for different climates." The atmosphere in town is more acid and in the country more alkaline. Alcohol vapors enormously increase the action of light. The light complementary to the dye has more action. Blue, of course, tends to affect more dyes than the red. The most favorable condition for bleaching by sunlight is one which is hot, moist and alkaline. A dye is called fast if not materially altered on southern exposure under glass for one summer month.

65. Sheppard: Photo-Chemistry. Published 1914, Longmans, Green & Co., page 431.

Photolysis of dye-stuffs.

66. N. Potter: Trans. Am. Electrochem. Soc. (1907), **12**, 218.

Sunlight and corrosion of metal by different paints.

67. Plotnikow: Photochemische Versuchstechnik. Published 1912, Leipzig. Akademische Verlagsgessellschaft m. b. H. pages 192, 193, Laws of Dye Fading. Page 273.

Temperature Coefficient of Light Reactions and 13 references to the literature on the same.

68. Toch: Materials for Permanent Painting (1911).

69. Mees: Discussion of Ives' Paper on Light Filters for Use in Photometry. Trans. Ill. Eng. Soc. (1914), **9**, p. 996.

Research Laboratory,
National Carbon Co.,
Cleveland, Ohio.

DISCUSSION.

President L. Addicks: I think this is a very good example of the breadth of view our research laboratories are now taking. As I understand it, this is undertaken purely in the interest of widening the application of certain forms of carbon.

I suppose there is no such thing as a dye unaffected by light, and it seems we want some means for rapidly testing these matters instead of having to expose them for a couple of months at a time. That is more important, I think, than the absolute quality of the light used.

MAXIMILIAN TOCH (*Communicated*): I have read Mr. W. R. Mott's paper on the "Use of the Flaming Arc in Paint and Dye Testing" with a great deal of interest, and it is quite evident that his work is scientific and of great interest and value, but I must protest against the title, which is wrong, because the tests only show one paint, lithopone; all the other materials used are either dyed materials or dyes used in making of lakes.

The fundamental difference between a lake and a paint is that a paint is opaque and a lake is translucent, and dyes as a rule are precipitated on transparent and translucent bases and used for coach color work, high grade enamels, printing inks and for decorative uses in table oil cloth.

It is of singular interest to note that Mr. Mott has proved the Bancroft-O'Brien theory of the darkening of lithopone. There was no doubt in my mind in the very beginning that the new theory as advanced was correct, and threw a light on the subject which will enable us at some future day to make a light-proof lithopone.

I regret that Mr. Mott did not examine my work which was delivered while I was the president of the section on "Paints" before the Eighth International Congress of Applied Chemistry, which deals entirely with the action of sunlight on both paints and lake colors, and it would be of very great interest to know what the action of the flaming arc is on such pigments as madder lake, and the toluodine and paranitraniline reds, which have always been regarded as permanent when not diluted with bases with which they may possibly react.

Mr. Mott is to be complimented on the extensive work that he has done, and I am frank to admit that additional work will be of great interest, particularly upon the solid pigments which react in sunlight, and become considerably darker, especially when they are mixed with lead and manganese catalyzers.

E. W. Lutus (*Communicated*): The arrangement and preparation of this paper reflect a great amount of credit due Mr. Mott for the immense amount of work and care which has been exercised in conducting such tests and investigations.

I believe that the various points which have been demonstrated and led up to the conclusions outlined, fully justify the efforts which Mr. Mott has made.

In the manufacture and sale of paints, varnishes and other allied lines of products, we are dealing with a very complex lot of chemical actions and reactions, and as our investigations progress we realize more and more fully that the actions of light and temperature, either singly or combined, play a very important part, and I am sure that these are factors which are entitled to far greater consideration and study than has been intelligently and systematically applied up to this time.

Judging from various phases of difficulties which we have encountered, and from such knowledge as we have of Mr. Mott's line of investigations with a view of utilizing the flame arc, I believe that this will prove to be a useful method and of considerable value in our line of work.

E. C. Holton (*Communicated*): We have been very much interested in the results obtained by Mr. Mott and have used the white flame arc in our laboratory in testing various pigments and paints, etc. In the cities like Cleveland, located in the Great Lakes region, there are many days in the year when the sunshine is very feeble and its bleaching effect on pigments, paints, oils and varnishes is very slight. At such times the use of the white flame arc gives promise of being extremely valuable since it will enable us to carry on accelerated tests otherwise impossible.

The best form of cabinet in which the tests are to be made has not yet been thoroughly worked out, but consideration must be given to temperature, moisture content of air, and possible presence of ozone and other active gases. Plans are now being developed for the use of this light in the bleaching of oils and varnishes on a commercial scale.

President L. Addicks: The paper does not involve any theoretical consideration. It is purely a practical application of several forms of arc light.

J. W. BECKMAN: It is pleasing to see some firm devise new uses for their products. I have had considerable correspondence with some firms, and it is almost impossible to get past the sales department. The narrow-minded attitude of many sales departments, who want the investigator to pay for any changes in the material when new uses are being tried out, often prevents new applications for old materials from seeing the light. The spirit of the company developing this material is highly to be commended, and an example for other new industries to follow.

SECRETARY J. W. RICHARDS: We seldom realize the variability and unreliability of sunlight when used for accurate testing purposes.

I have heard it stated that for certain kinds of color matching and testing you can use sunlight for only two hours a day, and the rest of the day it is not available. This general idea of substituting for a natural phenomenon some apparatus which gives constant and reliable and reproducible testing conditions, is something which can be followed with profit in other lines as well as in this one. It strikes me as a great advance in testing of these colors.

M. LUCKIESH (*Communicated*): Mr. Mott has contributed a valuable paper for those interested in color. It appears to me that there should be considerable interest in the spectral side of the problem. That is, a careful analysis of the effect of various parts of the spectrum on various dyes should add valuable data. In my own work I usually attempt to ascertain the effective region in the spectrum which causes fading of a given dye.

Inasmuch as there is considerable interest in the unstability of lithopone, some results recently obtained may be helpful. I attacked the problem of finding an artificial illuminant that would be effective enough to be used for keeping a check on lithopone products. It was soon learned that the near ultra-violet region between 0.3μ and 0.4μ was most effective for the illuminants considered, namely the magnetite, iron, and quartz-mercury arcs. The image of the filament of a gas-filled tungsten lamp was focused upon a lithopone surface for hours without producing any blackening effect. The spectrum of a quartz-mercury arc produced by a quartz optical system was focused on the lithopone

surface with the result that the lines between 0.30μ and 0.35μ were most effective. Both the iron arc, made especially for experimental purposes, and the magnetite arc were found to be very efficient in producing blackening. In both cases the sample became perceptibly gray in a few minutes. I had the same general experience with heat as described by Mr. Mott. Usually a fan was used to keep the sample cool.

The most efficient method of testing lithopone appears to be to focus an iron arc (or other effective source) upon the lithopone surface by means of quartz lenses. Blackening was produced by this method in a few seconds. Of course the irregularities in the operating of the arc are troublesome but these can be eleminated by various means. Various results obtained by Mr. O'Brien were also checked.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, in Joint Session with the American Institute of Electrical Engineers, September 17, 1915, President J. J. Carty (A. I. E. E.) in the Chair.

OVERHEAD ELECTROLYSIS AND PORCELAIN STRAIN INSULATORS.

By S. L. Foster.[1]

Abstract of Paper.[2]

There is a slight leakage of current from trolley wires to earth through insulated supports on all electrical overhead construction, which if not checked permits a flow of current which gives rise to electrical separation of water into oxygen and hydrogen. The oxygen liberated acts vigorously upon the adjacent metal parts which in time become badly corroded. This electrolytic action also seems to remove the galvanizing from live metal parts before attacking the iron. A partial remedy for this rusting of live galvanized wire is painting.

This electrolytic effect is also seen to take place over strain insulators where the creepage distance is insufficient. This indicates that a creepage distance proportional to the conditions met must be secured to stop the flow of current around the outside of the insulators. The author concludes that, under fog conditions, the insulator surface exposed for creepage is insufficient in our present standard devices.

Another form of overhead electrolytic action noticed in electric railway work is caused by use of dissimilar metals in contact. Sulphuric acid and other fumes in the air, and ozone from a nearby ocean, are supposed to be the electrolytes that set up a local battery action at these points of contact. The logical remedy for this trouble is to use similar metal in contact. The paper then describes the troubles encountered in San Francisco due to these causes, and the remedies which have been applied.

[1] Member American Institute Electrical Engineers.

[2] The full text of the paper will be found in the Transactions of the American Institute of Electrical Engineers.

DISCUSSION.

L. W. Webb (*Communicated, read by Mr. J. H. Finney*): I enclose small samples of copper-clad wire. This wire has been used on radio-antennæ on shipboard, and has proven entirely unsatisfactory for this use. It lasts from three months to a year maximum, and often not as long as three months. When once installed and not taken down it lasts the maximum length of time; but if disturbed after being installed the individual strands are found to be broken throughout the entire length, and the least twist or kink breaks the completed wire entirely. Where installed close to the smoke stacks on vessels the escaping gases cause rapid deterioration, and cases have been noted where the wire lasted only about two or three weeks.

This wire being exposed to a salt air atmosphere in combination with the gases escaping from the smoke stack apparently causes a very active chemical compound and the rupture of the outer copper casing, as these samples show. There are evidences of both chemical and electrochemical action. The high frequency currents circulating only in the outer skin of the copper enclosing jacket apparently produce from moist air small amounts of nitrous and nitric acid. The nitric acid attacks the copper jacket and destroys it, allowing electrochemical action between iron and copper, and thus completes the destruction of the wire itself. Also, smoke-stack gases in combination with salt air, rain, etc., and the high frequency discharges from antennæ produce, it is believed, both hydrochloric and nitric acids, which attack copper very virulently. Under certain circumstances it is believed it is possible to produce sulphuric acid also, but the action of nitric acid is believed to be the most plausible of all.

The copper-clad wire is the only one ever used, as far as I know, that proved utterly unsatisfactory in such a short time. Before trying this copper-clad wire we used a wire made up of seven strands of No. 20 B & S silicon-bronze wire and experienced very little trouble due to corrosion. The wire would, however, kink very readily, and when kinked would often break, but when properly handled no trouble was experienced. Since trying the copper-clad wire we are again using this silicon-bronze wire.

PRESIDENT L. ADDICKS: I think Mr. Webb's trouble in the case of the copper-clad wire seems to be due to the nitrogen of the atmosphere being oxidized by the discharge of the radio-antennæ, which pits the copper and you meet with galvanic action, have a salt solution for an electrolyte, and the iron anode and copper cathode which will very rapidly corrode. That problem is different from that presented in Mr. Foster's paper, where we do not have the high voltages to deal with, but it seems that the salt is largely the offender in furnishing the electrolyte.

I had intended to ask Mr. Foster why we could not calorize some of these connections with the idea of having aluminum surfaces to act as an anode, which would oppose the passage of any current, just as it does in the rectifier, but I am afraid, in the presence of the salt fog, the aluminum itself would be attacked by the chlorine, and that leaves us worse off than before. I suppose this salt fog is really ocean spray with considerable chlorine in it. I clipped from a newspaper the other day a reporter's view of this action:

"The disintegrating action of electrolysis from the electricity in salt water and salt air has given yachtsmen a good deal of trouble of various kinds. Aluminum utensils, for example, were most used for a time in the table services of yachts, as they were light, stood rough wear, and looked almost as well as silver. But it was presently discovered that overnight they became covered with a fine powder due to the action of the electricity in the salt air."

Omitting the witchcraft, I expect that is my own explanation, but would ask Mr. Foster regarding it.

S. L. FOSTER: We have not had much experience with aluminum in this city because when tried twelve years ago on a small scale near the Golden Gate it proved unsatisfactory in the salt foggy exposure. There was some small-sized bare solid aluminum wire put up around the cliffs by the telephone company as an experiment. It broke after being up only a few weeks. Upon examination it was found that this wire was badly tarnished and broke off upon being bent once 90° between the fingers. It had become brittle since its exposure. This tarnishing was probably due to the action of the chlorine content of the salt in the ocean spray.

Professor J. W. Richards tells us in his book that aluminum is readily acted on by chlorine.

Speaking of the copper-clad wire I would state that under the same conditions it went about as fast as the aluminum. The electric battery action appeared here, I assume that the electrolyte was hydrochloric acid formed from the chlorine in the salt moisture. It was probably not nitric acid, as there would not be enough stray voltage from a telephone line to produce nitric acid from the atmosphere. The iron salt formed burst the copper covering open before the wire broke. You could see this progressive action very clearly, splitting off the copper sheath both ways from various centers. Lead-covered cables and insulated copper wire are now used in this exposed district.

The manufacture of copper-clad wire has been abandoned, I understand.

Bare copper exposed near the ocean becomes covered with a greenish salt which I have assumed to be the oxy-chloride of copper. By others it has been called the carbonate of copper. I know of no analysis having been made of this salt.

John B. Fisken: An interesting part, to me, in Mr. Foster's paper was where he described the attacking of the span wires. I had occasion not long ago to look up the life of guy wires over railroad tracks in connection with some rules that were being gotten up. I found that ordinary galvanized cables (I cannot tell what it was, now, because it had been up ten or twelve years, and we had lost the records of it) which had been up many years over a railroad crossing were absolutely in as good condition as when put up. The tensile strength was just as high, but I found that some of the span wires supporting the trolley wires, apparently of the same material, had a very short life. Where I come from we are something like 300 miles away from the sea, and at an elevation of 1,900 feet, so, of course, there is no salt fog, The reason for this trouble I could not discover anywhere, but in reading Mr. Foster's paper I concluded I probably had the solution of it. I presume that the smoke from the locomotives formed on the insulators would allow this leakage Mr. Foster speaks of, and the electrolytic effect of the direct currents on this wire is probably what is causing that wire to have such a very short life.

I propose, when I go back home, to do a little in the way of painting or treating span wires with oil to find out if that is the reason.

S. L. FOSTER: In response to what Mr. Fisken spoke of, I would advise, instead of painting the spans that he put in longer insulators. The action referred to is probably due to the formation of sulphuric acid from coal burned in the locomotives.

Some coal contains large quantities of sulphur and its smoke forms sulphuric acid. This, emitted with the steam and smoke, would fit out the insulator with a nice electrolyte to begin the electrolytic action referred to.

JOHN B. FISKEN: The reason for the investigation was that very question; it was claimed that the sulphur contained in the coal would deteriorate these guy cables. We had to use galvanized steel for guy cables; it is not possible to use it for conductors, which we frequently had to put out on country roads. I have not had any analysis made of the smoke, but believe there is a large amount of sulphur in it; but it seems to me that would attack the guy wire as much as the span wire, which it does not seem to do. There must be an electrolytic effect somewhere.

JOHN H. FINNEY: I do not know a great deal about Pacific Coast conditions and their effect on aluminum; but in the East, aluminum wire which has been up in perhaps the worst town in the East for atmospheric conditions, Charleston, South Carolina, has been up about 14 or 16 years, to my personal knowledge, and is in very good condition today. There has apparently no change taken place in the aluminum. The middle strand of the 7-strand cable is just as bright as the day it was put up. I appreciate that west-coast conditions are not identical with the East conditions; they have not so much fog in Charleston, but have very bad atmospheric conditions, a heavily-laden salt atmosphere from the sea, and at times extremely dry heat. The other material on the railway line goes to pieces rapidly and corrodes. I am not defending aluminum when erected under wrong conditions. I want to make the point that perhaps our Eastern conditions are radically different from the Western conditions. There is a great deal of aluminum up in the coast, of course, and I presume most of it is in satisfactory condition, certainly many of the

big plants in California and elsewhere along the coast testify to its good qualities in respect to long-distance transmission work.

CHAIRMAN L. ADDICKS: I would ask Mr. Finney if it is not a fact that the aluminum he refers to as in use for a long time is on high-voltage transmission, where great care is taken in installation to avoid a leakage condition?

JOHN H. FINNEY: That is true, there is practically no leakage.

T. M. STATELER: I notice here a gentleman from the City Engineering Department, who got up the specification for some of the work of the Municipal Railway here in San Francisco, and I would ask him if he notices any particular leakage through his concrete poles. They used concrete poles in preference to metal poles.

PAUL J. OST: We have not had any concrete poles in service a sufficient length of time to give any real data upon them. However, we have had some experiences with a certain class of construction very similar to that which Mr. Foster describes. At our beach terminus, where we go within 200 feet of the ocean, we have had occasion within the last six months to take down a portion of the construction which had been up only eighteen months. Where the strand wire was met by the porcelain insulators all of the galvanizing was gone, and in most instances half of the strand wire had also been eaten away. In the case of a feeder span, the copper was badly eroded at the insulator. The loss of the galvanizing and of the strand wire itself does not extend back any great distance from the insulator, possibly not over an inch at the most, which to my mind indicates that it is an electrolytic action which is confined to the points where the current leaves the wire.

I might also add that we have had similar experiences with fire-alarm conductors in this same neighborhood. The wire, which is weather-proofed copper, is badly eaten off at the points where the tie wires are attached to it. I think this is also due to the electrolytic action of the current leaving the wire and going down the insulator. The potential in this latter case does not exceed 50 volts between the wire and the ground.

A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, in Joint Session with the American Institute of Mining Engineers, September 17, 1915, President L. Addicks in the Chair.

RADIOGRAPHY OF METALS.

By Wheeler P. Davey.

In an article in the General Electric Review, January, 1915, reference was made to the X-ray examination of a steel casting $\frac{9}{16}$ inch (14.1 mm.) thick. The object of this article was to describe in detail what has already been done in the way of an X-ray examination of a certain steel casting of which suspicion had been aroused as to its homogeneity when in the machine shop.

The original casting was 2½ inches thick and weighed about a ton. When received at the Schenectady Works of the General Electric Company it had been machined to approximately the desired shape and thickness. The amount still to be taken from the faces was not more than ⅛ inch (3 mm.) and in some places was only $\frac{1}{16}$ inch (1.5 mm.), but when this was removed it was found that some small imperfections had been cut into. These extended over an area about 5 inches (12.5 cm.) long and 1.5 inches (4 cm.) wide.

The mechanical department at once chiseled away a part of the surface at this point, and then sent the casting to the Research Laboratory to determine if, by means of an X-ray examination, it might be possible to reveal still other hidden blow holes or imperfections.

A Coolidge tube especially made for use on high voltages was set up in front of that part of the casting where the imperfections had been found. An 8 by 10-inch (20 x 25 cm.) Seed X-ray plate was mounted immediately behind the casting and the plate was backed by a large sheet of lead. The distance from the source of X-ray to the plate was 20 inches (50 cm.). The tube was excited by an induction coil with a mercury-turbine interrupter. The current through the tube was 1.25 milli-amperes and the potential across the terminals of the tube corresponded to that sufficient to break down a 15-inch (38 cm.) spark gap

Fig. 1. Radiograph showing flaw in center of casting. (The circle shows where the piece was later punched out.)

Fig. 2. Photograph of edge of punched button.

between needle points. The X-ray plate was exposed two minutes. At the bottom where the radiograph was taken, the finished casting was about $\frac{9}{16}$ inch (1.4 cm.) thick. In this way a number of exploratory radiographs were taken through different points of the casting, as, for instance, Fig. 1.

All the radiographs thus taken showed plainly the tool marks on the surface of the casting. All but one showed peculiar markings which were of such shape as to strongly suggest that they were indeed the pictures of holes in the interior. In the words of the surgeon it was decided "to confirm the diagnosis by making an exploratory incision." A circular piece, one inch (2.5 cm.) in diameter, was punched from the casting at a point where one of the radiographs indicated that a blow hole should be found. (Location of sample shown by circle on Fig. 1). Fig. 2 shows the end of the hole in the button thus punched.

This has proved, then, that with the proper X-ray exposure blow holes or cavities may be disclosed in apparently solid metal of considerable thickness. A careful comparison of the X-ray photographs and the button photographs leads to the conclusion that very small air inclusions are made visible; and the fact that the tool marks are plainly visible on the X-ray plate confirms this fact.

Since that article was written, it has seemed desirable (1) to obtain data from which the exposures necessary for any thickness of steel could be at once calculated, (2) to find the thickness of the smallest air inclusion which could be radiographed in a given thickness of steel, (3) to find the direction from which to hope for further progress, (4) to find the technique of radiographing metals.

In order to gain some preliminary data, several pieces of ½-inch (12.6 mm.) boiler plate were obtained, 5 by 7 inches (12.5 by 17.5 cm.) in size. In one of these, holes were drilled in such a way that the axis of each hole was midway between the faces of the steel and parallel to those faces. The diameters of these holes were as follows:

Hole Number	Diameter
1	¼ inch = 6.3 mm.
2	⅛ " = 3.1 mm.
3	$\frac{1}{16}$ " = 1.6 mm.
4	$\frac{1}{32}$ " = 0.8 mm.
5	$\frac{1}{64}$ " = 0.4 mm.

Exposures were made on Seed X-ray plates at 20 inch (50 cm.) distance with Coolidge tube X-117 operated on Scheidel-Western induction coil with mercury turbine break. The X-ray plate was placed on a sheet of ⅛-inch (3.1 mm.) lead. The steel was placed above this and a lead cover was placed over the whole in such a manner that the cover and backing made a complete lead-shield for the X-ray plate. (See Fig. 3). A rectangular hole in the cover allowed such X-rays as were able to penetrate the steel to reach the X-ray plate. This afforded complete protection against secondary rays. Without such precautions, the effect on the X-ray plate of secondary rays would have been greater than that of the rays used to take the picture. If the steel had been two or three feet (60 or 90 cm.) square, such

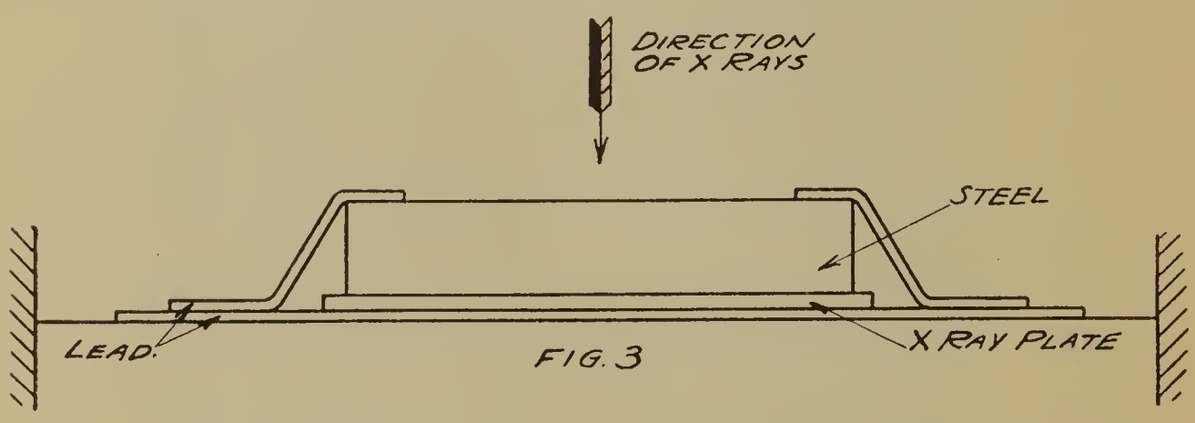

FIG. 3

precautions would have been unnecessary. By placing the pieces of boiler plate on top of each other, any thickness of steel desired could be obtained. Exposures were made at 11, 13 and 15 inch (28, 33 and 38 cm.) parallel spark-gap between points. An attempt was made to use a 17 inch (43 cm.) spark gap, but was abandoned due to flashing in the tube.

Results are tabulated below:

Thickness of Steel	Plate	Spark Gap Inches	Spark Gap Cm.	Exposure in MA-Min.	Holes Visible
½ inch = 12.5 mm.	D	11	28	7	1-2-3-4-5
	A	13	33	4	1-2-3-4-5
	B	15	38	2	1-2-3-4-5
1 inch = 25 mm.	E	11	28	45	1-2-3-4-5
	F	13	33	19	1-2-3-4-5
	G	15	38	10	1-2-3-4-5
1½ inch = 37.5 mm.	H	11	28	45	1-2-3 *very* faint
	I	13	33	30	1-2-3 very faint
	K	13	33	90	1-2-3 faint
	J	15	38	30	1-2-3-4-5 very faint
	L	15	38	60	1-2-3-4-5 faint

This really means, of course, that at 13 inch (33 cm.) spark gap 90 milliampere-minutes is sufficient to enable one to notice the difference in blackening between exposures through $1\frac{7}{16}$ inch (36 mm.) and 1½ inch (37.5 mm.), but is not sufficient to enable one to detect the difference in blackening between exposures through $1\frac{15}{32}$ inch (37 mm.) and 1½ inch (37.5 mm.) of steel.

The above results were necessarily incomplete, as the plates were by no means all of the same density. They served, however, to show two things:

FIG. 4 (a)

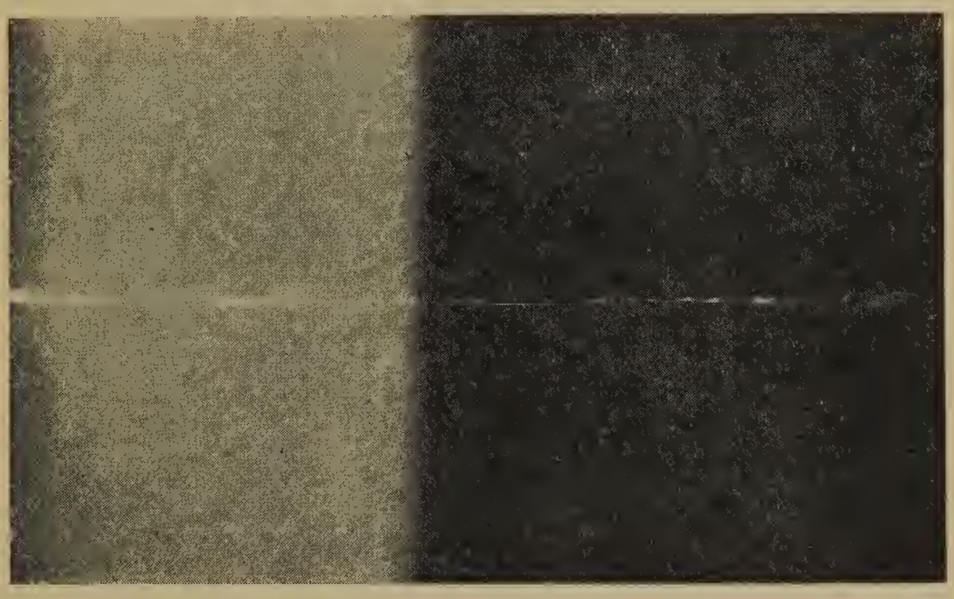

FIG. 4 (b)

(1) With the voltages which can now be used, it is impracticable to radiograph through more than 1½ inch (37.5 mm.) of steel with tungsten target tubes because of the time required.

(2) The use of high voltages does not seem to appreciably reduce the clearness of the picture obtained. (It was to have been expected from the published data on scattering in aluminum that enough scattered radiation would have been produced to blur the pictures, but plate B apparently shows as good detail as does plate D.)

It remained to confirm the above conclusions with data of a quantitative nature. Seed X-ray plates were therefore exposed

under the same conditions as before except that none of the slabs of steel used had been drilled. For each thickness of steel, all the exposures at a given spark gap were made on the same plate. Each plate, then, showed a series of steps which increased in density from one end of the plate to the other. Thickness of steel, spark-gap and milliampere-minutes were recorded on each plate by means of lead numbers. The following plates were thus exposed:

	Thickness of Steel		Spark Gap	
Plate	Inch	Mm.	Inches	Cm.
216	½	12.5	11	28
217	½	12.5	13	33
218	½	12.5	15	38
221	1	25	11	28
220	1	25	13	33
219	1	25	15	38
222	1½	37.5	15	38

A study of these plates showed the following facts:

Let $E_{0.5}$ be the exposure in milliampere-minutes necessary to produce a given darkening of the plate through ½ inch (12.5 mm.) of steel, and let E_1 and $E_{1.5}$ be the exposures necessary to produce the same darkening through 1 inch (25 mm.) and 1½ inch (37.5 mm.) respectively. Then at 11 inch (28 cm.) gap

$$E_{0.5} : E_1 = 1 : 11$$

At 13 inch (33 cm.) gap

$$E_{0.5} : E_1 = 1 : 8$$

At 15 inch (38 cm.) gap

$$E_{0.5} : E_1 = E_1 : E_{1.5} = 1 : 8$$

Also, through both ½ inch (12.5 mm.) and 1 inch (25 mm.) of steel

$$E_{13\ \text{inch (33 cm.) gap}} : E_{11\ \text{inch (28 cm.) gap}} = 1 : 4$$

and

$$E_{15\ \text{inch (38 cm.) gap}} : E_{13\ \text{inch (33 cm.) gap}} = 2 : 3$$

It is at once evident that *either* X-rays from a tungsten target at 13 inch (33 cm.) gap are more penetrating than when produced at 11 inch (28 cm.) gap, *or* the X-ray plates used are more sensi-

tive to the rays produced at 13 inch (33 cm.) gap. There is other evidence to show that the first of these conclusions is the more probable, but it is the *effect of the X-rays on the plate* which is of prime importance in this work, so that from a radiographic standpoint we may say in any case that the *effective penetration* of the rays is a little greater at 13 inch (33 cm.) gap than at 11 inch (28 cm.) gap.

In the same way we may conclude that the effective penetration at 15 inch (38 cm.) gap is the same as at 13 inch (33 cm.) gap.

FIG 5 (a)

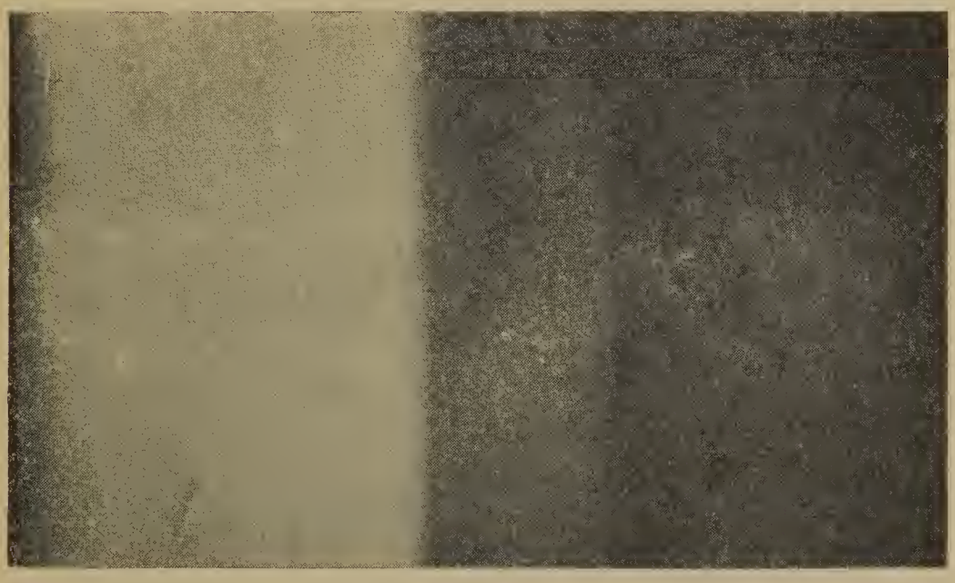

FIG. 5(b)

There is, however, a marked decrease in the amount of exposure required as the voltage across the tube (as measured by the spark gap) is increased. This may be due to one of two causes, *either* the efficiency of transformation from the kinetic energy of the cathode stream to the energy of the X-rays may be greater at high voltages, *or* there may be some peculiarity in the wave-form produced by the induction coil such that a great deal of energy is given off at a voltage corresponding to 13 inch (33 cm.) gap when the coil is operated so as to give a maximum voltage corresponding to a 15 inch (38 cm.) gap.

From the data at hand it is easily possible by well known

means to construct formulæ for computing the exposure necessary for radiographing steel at various spark gaps.

Let Q_0 be the quantity of X-rays impinging on the steel during the exposure.

Let Q be the quantity of the rays which pass through the steel.

Let x be the thickness of the steel.

Let λ be the coefficient of absorption.

Then if the X-rays are homogenous,

$$Q = Q_0 \epsilon^{-\lambda x}$$

where ϵ is the base of natural logarithms.

Now at 15 inch (38 cm.) gap we know that

$$\frac{E_{0.3}}{E_1} = \frac{E_1}{E_{1.5}} = 1/8$$

The rays given off at 15 inch (38 cm.) gap are therefore practically homogeneous. Since $E_{0.5}/E_1 = 1/8$ at 13 inch (33 cm.) gap, we may assume that these rays are also practically homogeneous. Rays given off at 11 inch (28 cm.) gap are still sufficiently homogeneous, after having passed through the first few hundredths of an inch (tenths of millimeters) of steel, to allow of being treated as though they were actually homogeneous. Calculations for exposures at 11 inch (28 cm.) gap are to be considered as being only good approximations.

For 15 inch (38 cm.) gap we have

$$Q/Q_0 = 1/8 = \epsilon^{-\lambda x} = \epsilon^{-0.5\lambda}$$
$$\log 8 = 0.5\lambda = 2.079$$
$$\lambda = 4.16 \text{ inches}^{-1} = 1.64 \text{ centimeters}^{-1}$$

Likewise for 13 inch (33 cm.) gap

$$\lambda = 4.16 \text{ inches}^{-1} = 1.64 \text{ centimeters}^{-1}$$

Applying the same method for 11 inch (28 cm.) gap

$$\lambda = 4.80 \text{ inches}^{-1} = 1.89 \text{ centimeters}^{-1}$$

Now at 15 inch (38 cm.) gap and 20 inch (50 cm.) distance 0.8 milliampere-minutes gives a good exposure through ½ inch (12.5 mm.) of steel. A corresponding darkening would have been produced on a bare plate by an exposure of 0.1 milliampere-

minutes. This corresponds to Q in our formula. We may therefore write, since $Q_0 = E$,

$$0.1 = E\,\epsilon^{-4.16x}$$
$$10\,E = \epsilon^{4.16x}$$
$$\log_\epsilon 10\,E = 4.16x$$
$$\log_{10} 10\,E = 1.80x$$
$$E = 1/10 \times \log_{10}^{-1} 1.80x$$

where x is the thickness of the steel in inches

or

$$E = 1/10 \times \log_{10}^{-1} 0.71x$$

FIG. 6 (a)

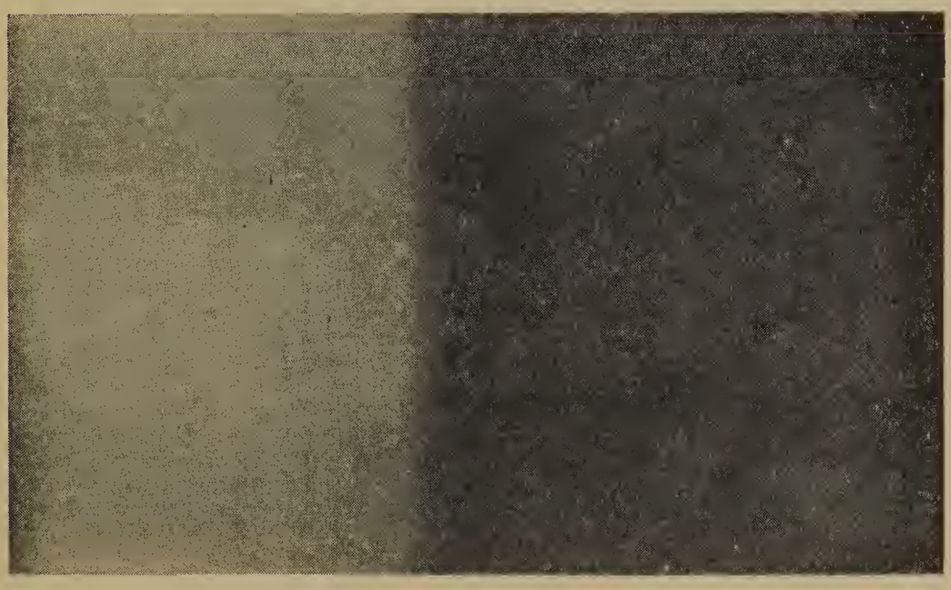

FIG. 6(b)

where x is the thickness of the steel in centimeters.

The corresponding formulæ for 13 inch (33 cm.) gap are

$$E = 3/20 \times \log_{10}^{-1} 1.80x \text{ (x in inches)}$$
$$E = 3/20 \times \log_{10}^{-1} 0.71x \text{ (x in cm.)}$$

The approximate formulæ for 11 inch (28 cm.) gap are

$$E = 3/5 \times \log_{10}^{-1} 2.09x \text{ (x in inches)}$$
$$E = 3/5 \times \log_{10}^{-1} 0.82x \text{ (x in cm.)}$$

It remained to find the thickness of the smallest air-inclusion which could be radiographed in steel at 15 inch (38 cm.) gap. For this purpose two plates of steel were taken. The faces were machined flat and in one of them a slot was cut, thus giving a *wedge* of air. The slot and the faces of the steel plates were then ground smooth. When completed, each plate was ⅝ inch (15.5 mm.) thick. The air wedge was 10 inches (25 cm.) long, 1 inch (2.5 cm.) wide and 9/64 inch (3.6 mm.) thick at its thick end. When the two plates were bolted together, the air wedge simulated a blow-hole in a casting. The wedge was then radiographed at 15 inch (38 cm.) gap. When the X-ray plates were dry the place was noted at which the outline of the wedge was barely visible. In order to avoid error, only a small portion of the wedge was viewed at one time, the rest being blocked off with cardboard. It was found that an air inclusion 0.021 inch (0.5 mm.) thick could be detected in 1¼ inches (32 mm.) of steel. In ⅝ inches (15.5 mm.) an air inclusion of 0.007 inch (0.2 mm.) could be detected.

Besides the work above outlined, a great deal of work has been done in the actual taking of pictures, so that the technique of radiography through metals might be worked out.

A record of a single example will suffice. Four samples of autogenous welds in steel were obtained. The welding had been done with an oxy-acetylene flame. The samples were ½ inch (12.5 mm.) thick and about 4 inches (10 cm.) square. The faces were fairly rough. Sample No. 1 had been welded on the surfaces only. (See Fig. 4a). Sample No. 2 had been insufficiently heated so that there was incomplete fusion of the metal at the center. (See Fig. 5a). In welding sample No. 3 an excess of oxygen had been used in the flame, causing the presence of oxide on the surface. (See Fig. 6a). Sample No. 4 was considered to be a good weld. (See Fig. 7a). One-half of each face was machined off, so that half the length of the weld was between flat; parallel faces; the other half was left under the original rough surfaces. As a result, one-half of each sample was ½ inch (12.5 mm.) thick and the other half was about ⅜ inch (9.4 mm.) thick. Radiographs were taken at 15 inch (38 cm.) gap under the conditions described above. Reference to the formula for exposure at 15 inch (38 cm.) gap shows that

the exposures through the ½ inch (12.5 mm.) and ⅜ inch (9.4 mm.) portions were in the ratio of 1 to 1.7. The resulting radiographs are shown in Figs. 4b, 5b, 6b and 7b.

Fig. 4b shows clearly the unwelded center of sample 1 in both portions of the picture. Fig. 5b shows, in both portions of sample 2, the holes caused by the metal not having been thoroughly fused at the center. That portion of Fig. 6b which was taken through the machined end of the weld of sample 3 would seem to indicate a porous structure. Such a structure was evident

FIG. 7(a)

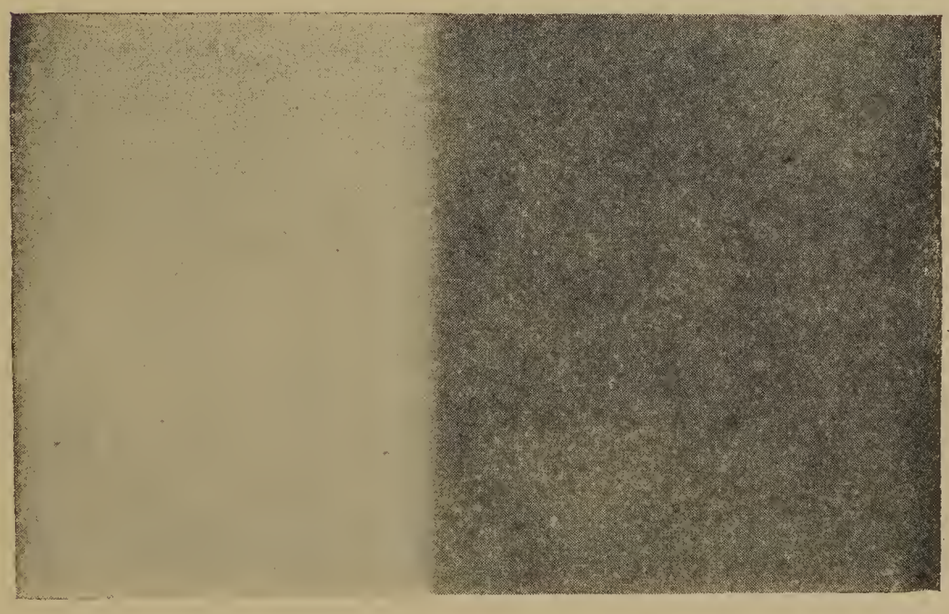

FIG. 7(b)

during the machining. The portion of the picture taken through the unmachined end of the weld did not show such a structure with certainty. This was to have been expected, as the inequalities in thickness due to the uneven surface were at least as great as those due to porous or frothy structure. Fig. 7b shows that as far as gross structure is concerned, sample 4 was a good weld.

It is of course self-evident that a radiograph gives only the gross structure of the metal, and gives no information as to the "grain," crystal interlocking at the edge of the weld, etc. A radiograph does, however, give valuable information as to the

presence of blow-holes, slag inclusions, porous spots and defects of like nature, which could not be found otherwise except by cutting into the metal. Unfortunately, no fluoroscopic screen now known is sensitive enough for this work; all work in metals must be done radiographically. An inspection of the formulas derived above makes one feel that, for the present at least, radiography of steel is a commercial possibility only up to thicknesses of ½ inch (12.5 mm.). For greater thicknesses, the time required is rather large. The great saving in time which is gained by the use of 15 inch (38 cm.) spark-gap instead of 13 inch (33 cm.) gap makes it seem probable that a further increase in the voltage across the tube would allow one to radiograph still greater thicknesses of steel.

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A paper presented at the Twenty-eighth General Meeting of the American Electrochemical Society, in San Francisco, September 16, 1915, President L. Addicks in the Chair.

THE COLLECTION OF RADIUM EMANATION AND ITS PREPARATION FOR THERAPEUTIC USE.

By Rowland S. Bosworth.*

In the use of radium as a therapeutic agent three general methods are available. First, the radium salt itself may be applied directly in various forms of applicator or may be injected into the body either locally or intravenously. Second, the radioactive gas, radium emanation, produced by radium may be pumped off from solutions containing the stock radium supply, purified and introduced into tubes which in turn are used in therapeutic application. Third, the active deposit produced on objects by radium emanation, consisting of the elements Radium *A*, Radium *B*, Radium *C*, may be collected on sheets of metal for use in local application, or solutions may be used of it for injection.

The advantages of the last two methods over the first are four: (1) The emanation or active deposit can be obtained in a much smaller volume than the radium salt with which it corresponds, and so is less clumsy to handle, a feature of great importance in parts of the body where space is limited. (2) The quantity of emanation in a given dose can be varied at will, but with the radium salt method one is confined to the use of tubes of invariable strength. (3) The injection of the active deposit is superior to the injection of radium salt, in that in the latter case a valuable material is permanently used up. Moreover, the injection of the salt itself is accompanied with some uncertainty, as the radium may be precipitated in some part of the body and continue its work indefinitely. (4) Finally, all risk of loss of radium through constant handling, by dropping, etc., is entirely obviated, a matter of great practical importance when one is dealing with a material of such scarcity and value.

The emanation and active deposit methods are, however, subject to a loss of a few percent of the emanation during the process

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of collection, an unimportant matter in view of the many great advantages of these methods. Moreover, they are methods which are not practicable on a small scale, since they require rather extensive apparatus, considerable active attention, and acquaintance with a somewhat complicated technique. It is not the purpose of this paper to expound any new scientific principles with regard to the collection of radium emanation, but to review the methods that have been proposed for that purpose and to show some of the practical details of the operation of one of these methods in the routine of every-day work in a hospital.

Radium salts in solution produce, besides radium emanation, other gases consisting of water vapor, hydrogen and oxygen formed by the decomposition of water under the influence of the rays, carbon dioxide formed by the action of the rays on traces of organic matter, such as stopcock grease, and helium, the product formed when the *alpha* particles lose their charge and velocity. In order to collect the emanation in small volume suitable for use, it must be purified from these gases. The best known and oldest method for accomplishing this is that devised by Ramsay and now largely used in England, notably at the Radium Institute of London. In the operation of this method the radium salt is kept in solution in water and the space above the liquid is exhausted free from air. At intervals the collected gases are allowed to expand into an exhausted vessel. Hydrogen and oxygen are removed by causing their chemical union by means of a spark. Water is removed by phosphorus pentoxide, and carbon dioxide by introducing the gases into an exhausted tube containing a small piece of caustic potash. The remaining gases consisting of emanation, helium and a small amount of hydrogen are passed into a tube surrounded by liquid air. The emanation is thereby condensed to a liquid and the uncondensed hydrogen and helium are pumped off by a mercury pump. The emanation is then vaporized again by warming the tube, transferred by mercury into whatever container is desired, and sealed off.

The other method of purifying radium emanation is that devised in Curie's laboratory by Duane. The gases collected over the radium solution are allowed to expand into an exhausted tube with which are connected three tubes containing respectively

sodium hydrate, phosphorus pentoxide, and a copper wire coated with copper oxide and so arranged, by connecting with platinum wires sealed through the glass of the tube, that it may be heated to redness electrically. Of the collected gases, carbon dioxide, hydrogen, oxygen, water vapor, helium and emanation, the first named is removed by the sodium hydrate. The hydrogen and oxygen are caused by the heated copper wire to unite to form water, the excess of hydrogen being taken care of by the coating of copper oxide. Then the total water vapor is removed by the phosphorus pentoxide, leaving only helium and emanation. These are transferred together into capillary tubes and sealed off, no attempt being made to remove the minute amounts of helium unless the emanation is desired for some special physical work in which the presence of that element would be objectionable.

The advantage of the first method lies in the extremely pure product which may be obtained. However, the volume of the mixed helium and hydrogen obtained by the Duane method is sufficiently small for practical therapeutic work. The practical disadvantages of the Ramsay method consist in its requiring liquid air (a product not always available) for the removal of part of the hydrogen, and in the fact that the purification of the emanation by condensing with liquid air is essentially a fractionation and connected therewith there is a necessary small loss of emanation which passes off with the uncondensed helium and hydrogen. The simplicity of operation and the high percentage of emanation recovery were advantages which decided in favor of the Duane method for our work.

After purifying the emanation in the manner described, its subsequent treatment is determined by the use to which it is to be put. If it is desired to apply it directly to a tumor growth (the commonest way in which it is used), the emanation is transferred by mercury to glass capillary tubes having an outside diameter of 0.3—0.4 mm. with an inside diameter of 0.25—0.35 mm., and these are hermetically sealed with a small flame. In preparing these for application, a number sufficient to give the quantity required are introduced into lead or silver containers shaped appropriately for use in different parts of the body. If it is deemed wise to imbed emanation in the tumor mass, these tubes, or the emanation itself, are sealed by means of wax into

a hypodermic needle, and the needle is used by sticking into the tissue and leaving for a period of time.

If one wishes to make an application of the active deposit from radium emanation instead of the emanation itself, a hollow cylinder formed of sheet lead is introduced into a glass tube of such size that the cylinder fits closely the inside of the tube. The whole is sealed into the collecting and purifying apparatus, exhausted with a mercury pump, an appropriate quantity of emanation is transferred by mercury into it, and allowed to stand three hours. The emanation can be then transferred to some other container and the lead cylinder containing a coating of the active deposit on the inside can be removed from the tube, flattened out, and used for application. For injection purposes, the emanation is left in contact with a small amount of common salt for three hours, as above described for the sheet of lead. The salt is then dissolved in a few c.c. of water and the solution containing whatever quantity of active deposit one wishes is injected as desired. As the activity of the active deposit decays to zero in about three hours its action does not continue indefinitely, as would be the case if the radium salt were itself injected.

The question of the filtration of the rays from radium is a very important one from a therapeutic point of view. The *alpha* rays have such a low degree of penetration that they cannot reach tissue to a depth sufficient to be of value. Consequently they are always removed by placing a covering around the application, say a sheet of lead about 0.1 mm. thick. For the treatment of pathological conditions on the surface of the body the *beta* rays can be used, and in that case no further filtration is required. However, if the lesion to be treated is of a deep seated nature, the *beta* rays will not penetrate to a sufficient depth and are rather harmful than valuable, producing an inconvenient and painful burn upon the skin before the deeper tissue is sufficiently treated by the *gamma* radiation. In this case the container is made of lead or silver, 1 to 2 mm. thick, to absorb the *beta* rays and allow the *gamma* rays to pass through. In using the *gamma* rays, it is necessary to remember that on passing through metals they produce easily-absorbed rays of the *beta* ray type, which must be filtered out. This is done by covering the applicator with a sheet of rubber 1.5 mm. thick.

The various problems of dosage are largely medical rather than physical in their nature and do not fall within the scope of this paper. It has been the author's object to show the advantages of the use of radium emanation in therapeutic work over the use of the radium salts themselves, to outline two methods for the collection and purification of radium emanation, showing the advantages of each, and, finally, to show the different principles involved in the different methods of using the emanation and the kind of filtration which is suitable in the different cases that may arise.

DISCUSSION.

President L. Addicks: The curative properties of radium are now reaching a sensible basis, and it is admitted to be of definite value. A paper of this kind is of educational value, and it shows the broad field belonging to this little Society, and which we cover. We have covered metallurgy, chemistry, physics, and now we are verging on medicine, and all during this brief morning session. We can say that wireless telegraphy belongs to us, as well.

Herman Schlundt (*Communicated*): The use of radium emanation for therapeutic purposes, instead of radium itself, marks a distinct advance in radium therapy. As Dr. Bosworth points out, the radiations from radium preparations that are primarily of therapeutic value consist of the penetrating *beta* and the *gamma* rays, and these are emitted mainly by the emanation and its short-lived decay products. Radium, the element and parent of the emanation, emits only *alpha* rays and *beta* rays of moderate penetrating power, no *gamma* rays: Hence there is no advantage in using radium except to insure a constant source of radiation; but inasmuch as the radium equivalent of a given dose of radium emanation can be deduced for any time after its separation, from its known rate of decay, no uncertainty need ever exist regarding the quantity of radiation with which one is dealing.

From the practical side, the great advantage in distributing the emanation instead of radium is the last one mentioned by Dr. Bosworth, namely the entire avoidance of risk of the loss of the radium, not only by handling and dropping, but loss in transit,

when the precious material is to serve different physicians. As the supply of radium increases and its therapeutic uses unfold, its efficient use and distribution will become a matter of growing importance. The distribution of the emanation instead of radium will greatly facilitate its more general use and practically obviate the risk of loss. Speaking then, not from the viewpoint of the expert in radium therapy, but as one greatly interested in the conservation of our radium supply, I venture to suggest the establishment of centers for the distribution of radium emanation, that is, Radium Banks as dispensatories of radium emanation. For example, from a radium preparation containing a gram of the metal, five tubes of emanation each equivalent in therapeutic value to nearly 200 milligrams of radium can be prepared initially, and then as the emanation accumulates a dose equivalent to 160 milligrams of radium can be separated daily thereafter for a good many years, as the half-life period of radium is nearly 2,000 years. The loss of one of these tubes of emanation would be relatively insignificant in comparison with the loss of its radium equivalent as the following simple calculation will show: Assuming that a gram of the element radium has a value of $125,000, and that its annual gross earning power is 20 percent, we see that the doses of emanation that are available daily should bring $25,000 during the year or about $70 per dose. Each dose, however, represents the equivalent of 165 milligrams of radium, and its value is well below one-half of one percent of the value of its radium equivalent.

The activity of the tubes of emanation falls off relatively fast and according to a simple law of decay, and their radium equivalent can always be deduced from the decay curve of the emanation. In the course of three weeks after separation of the emanation its activity is slightly more than 2 percent of its initial value, but even then the tubes are very serviceable as applicators, as Duane has pointed out, by fastening a number of them on a sheet of cloth.

Dr. Bosworth's summary of the methods of Ramsay and Duane for obtaining radium emanation for therapeutic use will certainly be of interest to the medical profession, and I have added a word in the hope that the medical societies will consider the establishment of Radium Banks in our larger cities for the distribution of radium emanation.

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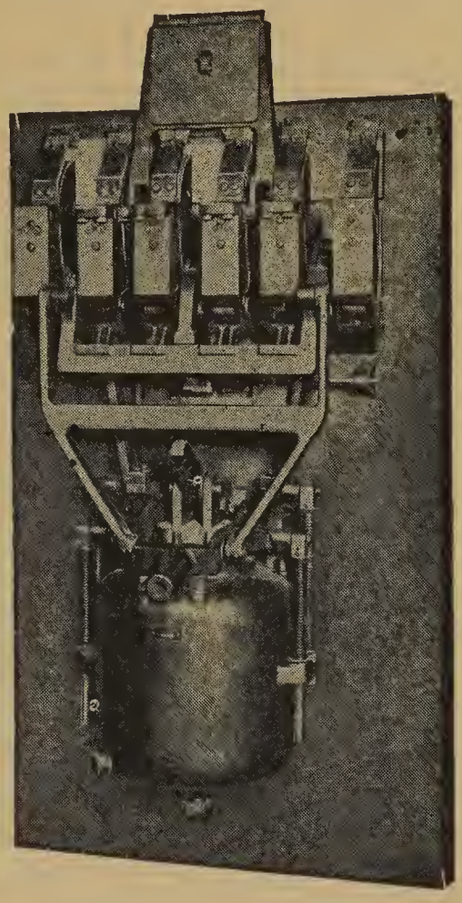

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